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Photograph by C. Hallam, Harpenden

DR. R. K. SCHOFIELD, 1901–1960

To the grief of his many friends Robert Kenworthy Schofield died on 8 June 1960 after an illness which was mercifully brief. He was then Reader in Soil Science at Oxford, President of Commission I of the International Society of Soil Science, and President of our British Society of Soil Science.

After graduating at Cambridge he studied under E. K. Rideal at Durham and in 1928 joined the Physics Department at Rothamsted. It was here from 1928 to 1956 that the greater part of his scientific work was done and it gained for him an international reputation.

He was able to illuminate any subject he touched and had a knack of using simple equipment to obtain decisive information. Even more influential than his many scientific papers were the encouragement and stimulus that came from his keen and positive appraisal of problems that otherwise seemed dull and unrewarding. He was generous at all times in giving courteous attention and helpful answers to those who sought his advice. He gained the affection and respect of his colleagues in this country and of visitors from overseas. We join in applauding his work and we deplore the passing of an outstanding scientist and our good friend.

THE STONY TABLELAND SOILS OF THE SOUTH-EASTERN PORTION OF THE AUSTRALIAN ARID ZONE AND THEIR EVOLUTIONARY HISTORY

R. W. JESSUP

(*Commonwealth Scientific and Industrial Research Organization, Canberra, A.C.T.*)

Summary

The stony tableland soils which are paleosols of Quaternary age have a clay profile, high proportion of exchangeable sodium, strong salinity, large amounts of stone in the upper few inches of the profile, a surface stone pavement, low carbonate but high gypsum contents and gypsum at shallower depths than carbonate. The surface of the soil layer has a gilgai micro-relief.

The soils formed on deposits of wind-blown clays. Underlying the soil layer is a discontinuous layer of wind-deposited gypsite. These wind-blown materials (called lakulangite) were derived from lacustrine sediments; deflation of these sediments led to the formation of wind-excavated hollows that are often of large extent.

Stones originally buried beneath the clay deposit have been moved upwards and concentrated on or near the soil surface.

Introduction

THE name stony tableland soils (Jessup, 1951) was applied to fine-textured, gypseous, and saline soils associated with plateaux ('tablelands') in north-western South Australia; they have an abundance of stone in the upper part of the profile and on the surface. Soils with these characteristics have also been called stony desert tableland soils (Stephens, 1956).

In a previous paper (Jessup, 1960*b*) the lateritic soils of the south-eastern portion of arid Australia, to which a Pliocene age has been tentatively assigned, were discussed; the laterites are restricted to remnants of an ancient land surface. Following the development of the laterites and prior to the formation of the stony tableland soil layer there was a period of major erosion which resulted in the formation of the younger land surface above which the lateritic plateaux rise.

The present discussion is concerned with occurrences of stony tableland soils in two extensive areas in the south-eastern portion of arid Australia; the location of these areas and the environment of the region have already been discussed (Jessup, 1960*a*). The distribution of the soils within the areas investigated is shown in Fig. 1.

The Characteristics of the Soils

The surface of the stony tableland soil layer has a well-developed micro-relief due to the presence of scattered irregular-shaped depressions (Plate I, Fig. 1). On sloping ground each depression has a mound along its lower margin. The depressions are commonly 3 to 10 yds. across and 6 to 24 in. deep, while the mounds are 6 to 18 in. high. The depressions are separated by flats ('shelves') which may vary from 4 to 35 yds.

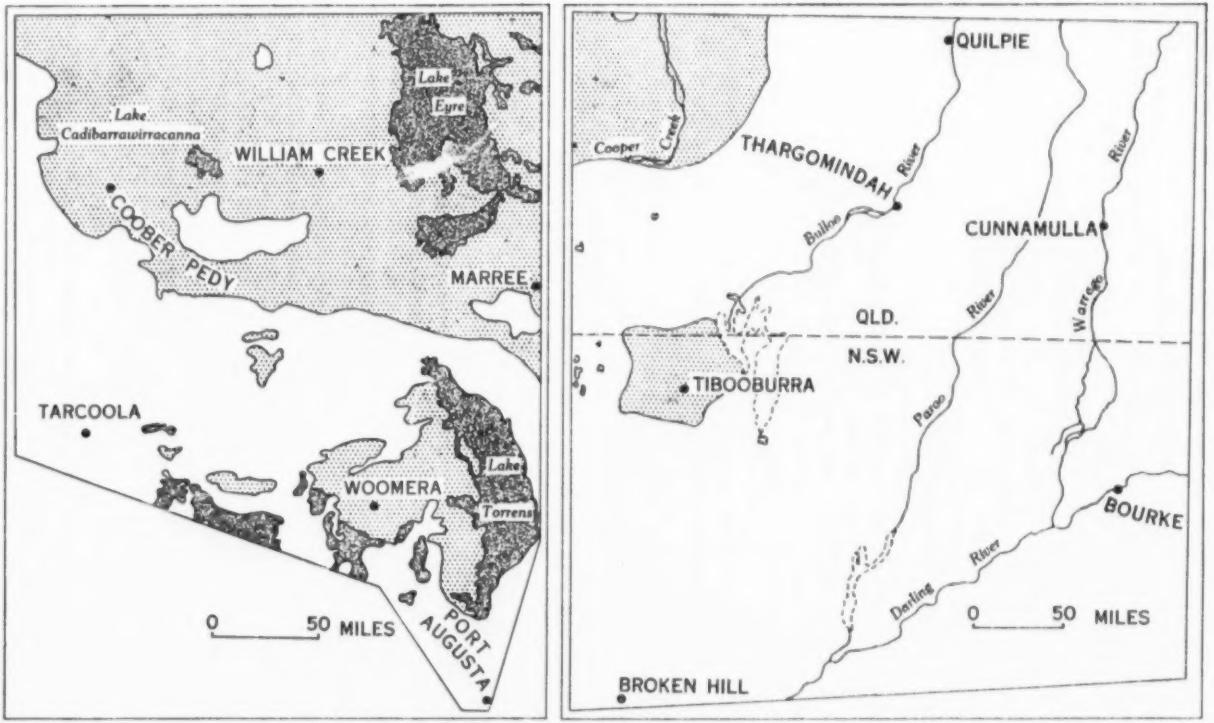

FIG. 1. Showing the distribution of the stony tableland soils in the two areas studied.

across. The term 'gilgai' is used in Australia for this and other similar kinds of micro-relief.

The shelf and mound soils have a well-developed surface stone pavement, large amounts of stone in the upper part of the profile and usually none at depth. In the depressions there are only a few stones on the surface—the stone is buried in the A and upper part of the B_1 horizon.

In most areas the stones consist of quartzitic silcrete derived through erosion of the lateritic plateaux (Jessup, 1960*b*); they are sub-angular and mostly ¼ to 6 in. in size, but occasional blocks of silcrete 3 ft. and more in length are found. On the Arcoona plateau, where the soils overlie quartzites, the stone pavement consists principally of flat plates of quartzite ½ to 1 in. thick and ½ to 18 in. long (Plate I, Fig. 2). Most of the stones have a well-developed 'desert varnish'.

The shelf profile has a vesicular apedal[1] surface horizon up to 2 in. in thickness that varies from reddish yellow (7·5 YR 7/6) to yellowish red (5 YR 5/6) in colour and from sandy loam to light clay in texture. The horizon has a sharply defined boundary, contains large numbers of stones, and has a soft to slightly hard consistence when dry and varies from non-plastic to plastic and non-sticky to sticky when wet.

The B_1 horizon varies from 5 to 12 in. in thickness and consists of clay or sandy clay with a moderately to strongly developed angular or sub-angular blocky structure with peds ¼ to ¾ in. in size. Colour ranges from reddish brown (5 YR 5/6) to red (2·5 YR 4/6). This horizon is normally non-calcareous but contains a large number of pockets and veins of micro-crystalline gypsum. Stone content is variable (absent to moderate). The clay has a hard consistence when dry and is sticky and plastic when wet.

There is a diffuse boundary with the B_2 horizon which is apedal, 12 to 60 in. in thickness (sometimes more) and clay or sandy clay in texture. Colour ranges from reddish brown (5 YR 5/6) to red (2·5 YR 4/6). This horizon contains a large number of pockets of gypsum and variable amounts of carbonate; the latter may be absent or there may be a small amount in the fine earth in a zone within the horizon. Consistence is hard to very hard when dry and very sticky and plastic when wet. Stone is usually absent.

The soil in the depressions has a similar profile but there are structural differences. Thus the A horizon of the depression soil may be laminated or apedal while the B_1 horizon has a moderately developed sub-angular blocky structure with ½ to 1½ in. peds. Cracks up to an inch in width extend from the surface into the B_2 horizon when the soil is dry.

The soil associated with the mounds is again similar to the shelf soil. However, the shallow A horizon has a weakly to strongly developed multi-angular blocky structure consisting of ⅛ to ½ in. peds.

All of the soils are saline. Total soluble salt contents are highest in

[1] 'The term apedal is used for soil that is structureless; its use avoids the contradiction of stating that the structure of a given soil is 'structureless' (see Butler, 1955, *Jour. Aust. Inst. Agric. Sci.*). All Munsell colour notations refer to dry soil. Consistence terms follow the system described in the U.S.D.A. Soil Survey Manual, Handbook No. 18, 1951.

the shelf where, even in the surface inch, soluble salt contents range from 0·06 to 2 per cent. At a depth varying from 6 to 12 in. from the surface, salt content rises to between 1 and 3·5 per cent. Mound and depression soils have between 0·04 and 0·06 per cent. soluble salts in the surface inch, increasing to between 1 and 2·5 per cent. at depths varying between 12 and 36 in. from the surface. Exchangeable cations have been determined on eight samples. The results show that, while calcium is the dominant cation throughout the shelf, mound, and depression soils, sodium constitutes 9 to 17 per cent. of the total cations in the top 6 in. of the profiles except in the mounds. In the surface of the mounds and also at depth in the shelf and depression profiles, sodium constitutes 21 to 25 per cent. of the total cations.

Detailed analyses of profiles have been presented by Crocker and Skewes (1941, soil type 1), Crocker (1946, 'brown soils associated with surface gibbers'), Jessup (1951, Arcoona and Coober Pedy soils), and Jackson (1958, Wertagunyah type 1).

The Origin of the Parent Materials

Underlying the soils and separated from them by a sharply defined boundary is a discontinuous layer of powdery, unconsolidated gypsite. The gypsite consists of 75 to 86 per cent. of gypsum ($CaSO_4.2H_2O$), 1 to 1½ per cent. of calcium carbonate, together with clay. The gypsite layer is most commonly 2 ft., but may be as much as 6 ft., in thickness. In the Lake Eyre region, where they occur over very wide areas, the stony tableland soils usually vary from 1 to 2 ft. in depth and are commonly underlain by 2 ft. of gypsite.

The fine-textured soils and the associated gypsite layer overlie a variety of non-gypseous and non-argillaceous substrata including quartzite, sandstone, and quartzitic silcrete. They also directly overlie pallid zone materials exposed through truncation of lateritic soils (Jessup, 1960*b*) and shales and mudstones. It is, therefore, evident that the materials in the clay layer on which the soils developed and those in the gypsite layer are of extraneous origin. Furthermore, since the layers blanket the entire landscape, irrespective of relief, it is concluded that the materials were transported and deposited by wind.

It is suggested that the wind-blown clays and gypsite were derived through deflation of lacustrine sediments that had accumulated in, and were exposed as a result of the drying out of, ancient lakes, notably the vast Lake Dieri which has been discussed by Howchin (1913) and Mawson (1934). The Lake Dieri deposits have been examined in the Lake Eyre area (King, 1956) and in a number of other localities; it is significant that the uppermost sediments consist of highly gypseous deposits and that these overlie deposits of saline and gypseous clays.

An outstanding feature of the Lake Dieri lacustrine basin is the presence, within it, of large numbers of playa lakes. King (1956) showed that the Lake Eyre playa depression which is 4,000 square miles in area was formed as a result of removal, by wind, of a depth of at least 36 ft. of Lake Dieri sediments. Investigations have shown that Lake Frome and a large number of other smaller playa depressions are wind-excavated

hollows and it is likely that Lakes Callabonna, Blanche, and Gregory had a similar origin.

Moreover, deflation of the Lake Dieri sediments was not confined to the playa hollows, but occurred in surrounding areas (King, 1956). Jessup (1960*a*) has pointed out that 'islands' consisting of lacustrine sediments that have survived deflation frequently rise above the playa floors. Blackwelder (1931) has recorded similar residuals in the bed of a playa in the United States and has shown that the sediments between these residuals were removed by deflation.

There is strong evidence, therefore, that first gypseous and then clayey sediments were removed from the Lake Dieri basin (Fig. 2).[1] Evidence supporting the proposal that the parent material of the stony tableland soils was derived from these sediments has been obtained by fluorescence X-ray spectrography which shows that the stony tableland soil has a composition similar to the lacustrine clays (Fig. 3). The most convincing proof is the similarity with respect to trace elements.

Processes Involved in the Formation of the Soils

The soils have no carbonate in the A and B_1 horizons but there is frequently a zone of slight carbonate accumulation in the B_2 horizon. This indicates that, during their formation, the soils were subjected to sufficient leaching to allow of considerable movement of carbonate. The presence of abundant pockets of gypsum, and of chloride, above the zone of carbonate accumulation, has apparently resulted from subsequent redistribution (upward migration) of these soluble constituents.

The formation of the gilgai micro-relief is probably related to the presence of sodium clays which expand on wetting and contract and crack on drying. Leeper *et al.* (1936) postulated that soil cracking during the drying cycle is important, since at this stage some surface soil falls into the cracks, adding to the bulk of the material below. As a result of subsequent wetting and swelling, pressures are exerted upwards and sideways. The pressure is finally relieved at a point of weakness by upward movement of a block of soil to form the mound. This hypothesis is supported by Hallsworth *et al.* (1955). The presence of mounds on the downslope side of the depressions on sloping ground may be due to the fact that the stresses are more easily relieved in this direction.

Leeper *et al.* (1936) and Hallsworth *et al.* (1955) have shown that the soil exposed at the surface of the mounds has properties similar to the subsoil in the depressions; they attribute this to removal, by erosion, of the upper portion of the profile after the mound is formed. This may explain why the content of exchangeable sodium in the upper part of the mound profile in the stony tableland soils is comparable with that of the B horizon of the shelf and depression soils.

When rain falls, water accumulates in the depressions. As a result the zone of maximum soluble salt concentration is deeper in the depressions than the shelves.

Where the stony tableland soils occur they are present over the

[1] The name lakulangite (from lakulang, an aboriginal word for saltlake) is proposed for the wind-borne materials derived through deflation of the lacustrine sediments.

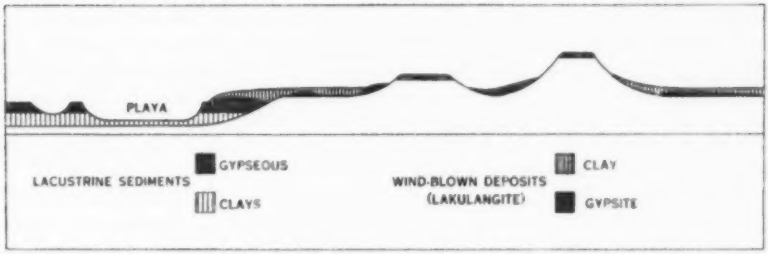

FIG. 2. Diagram illustrating the relationship between the Lake Dieri sediments and the wind-transported deposits. The present playa lakes occur in wind-excavated hollows within the lake sediments.

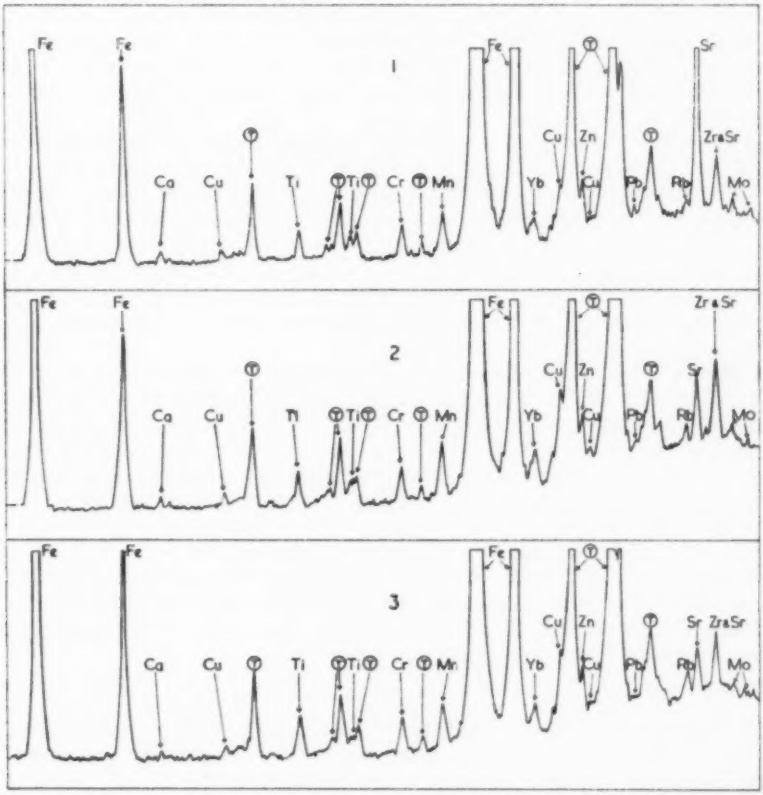

FIG. 3. Fluorescence X-ray spectrograms. 1, *in situ* lacustrine clay from Lake Dieri; 2, stony tableland soil from south of William Creek; 3, stony tableland soil from south-west of Coober Pedy. T is the tungsten target.

entire landscape, irrespective of relief. There are large amounts of stone in the upper portion of the soils and on their surface even in the highest sites. The stones in these situations could not have been transported and deposited by water during or after the formation of the soil layer but must originally have been present on the surface of the pediments on which the wind-blown lakulangite was deposited and their occurrence in the upper part, and on the surface, of the soils could only be explained if they had been moved upwards.

A simple experiment has been carried out to ascertain whether stones are moved upwards through stony tableland soil by repeated wetting and drying. Twelve stones varying from ½ to 1 in. in size were placed on the bottom of each of two 6-in. diameter crystallizing dishes. Stony tableland soil was ground to less than 2 mm. and added to the dishes until the stones were almost covered. The soil in one dish was then subjected to 22 wettings and dryings, a thin layer of soil being added before each wetting. The other dish (the control) received similar additions of soil and similar treatments but no water was added. Drying was carried out in a forced draught oven at 60°C. By the end of the experiment the depth of soil in the dishes was 1½ in. Displacement of the stones from the bottom of the dishes was then measured. All of the stones in the first dish had been moved, the maximum upward displacement being ⅞ in., while in the control the stones were still on the bottom of the dish.

In other dishes a similar procedure was adopted but the stones, at the commencement of the treatments, were buried beneath ½, 2, and 3 in. of soil respectively. Only the stones buried by ½ in. of soil were displaced, maximum upward movement being ⅛ in. The fact that movement only occurred under conditions of shallow burial suggests that the stones in the stony tableland soils may have been moved upwards during the accession of the wind-blown clay.

Springer (1958) demonstrated similar displacement of stones under experimental conditions and postulated that 'through swelling of the soil, the stone is lifted slightly. As the soil shrinks, cracks are produced around the stone and within the soil. Because of its large size the stone cannot fall into the cracks, but finer particles may either fall or be washed into the cracks. The net effect is an upward displacement of the stone.'

There are stones in the upper part of stony tableland soil profiles even where the soils are underlain by the gypsite layer. It is difficult to envisage that stones would have been moved up through the gypsite but, as already indicated, this layer is not continuous. Apparently some of the stones that were moved up through the clay were later transported downslope by water.

Discussion

The evolution of the soils involved a period when the parent material layer, consisting of wind-deposited materials, was formed and a subsequent period when the accession of these materials ceased and soils developed on the deposits that had accumulated.

Hallsworth *et al.* (1951) regarded the soils in the 'stony deserts' of New South Wales (including stony tableland and other soils) as being

formed under the influence of the present climate and suggested that the clay was derived from underlying argillaceous rocks. Thus, they say 'the high clay content of these soils in a low rainfall area (6 to 9 in. per annum) is explained by the observation that they are found always on rocks such as shales, slates or mudstones. Their clay has consequently been largely pre-formed in an earlier geological era . . .'.

However, it has now been shown that their clay profiles are explained by the fact that their parent materials were wind-blown clays. Furthermore, there are very extensive areas where the stony tableland soils were later destroyed by erosion leaving isolated occurrences (Fig. 1); it will be shown in a later paper that here two younger soil layers have developed and that sand ridges that form part of the older of these layers overlap, and are superimposed upon, the stony tableland soils in some localities. The latter soils, therefore, are relic features attributable to an earlier soil-forming period which, for convenience in later discussions, will be called the Andamooka period of soil formation.

Stephens (1956) suggested that the stony tableland soils are modified truncated residuals of former soils from which the upper horizons have been removed. No evidence in support of this hypothesis, except for the possibility of erosion of the upper part of the profile in the mounds, has been obtained during the present investigation. Upward movement of stones that probably occurred at the time the wind-blown parent materials were accumulating, that is, prior to the development of the soil profile, appears to have played a major role in the formation of the surface stone pavement but deflation may have aided its development.

The surface stone pavement now protects the soils from deflation as Hallsworth *et al.* (1951) and Jessup (1960*a*) have pointed out.

Accurate dating of the age of the Lake Dieri sediments has not been possible since the fossil fauna in the beds are a fresh to brackish water association. King (1956) tentatively postulated an early Recent age for the uppermost lake sediments (the gypseous and clayey beds). David and Browne (1950) also postulated that the lake dried out in the early Recent. Assuming this to be so, and as Lake Dieri must have been dry when the wind-blown materials were derived from its sediments, formation of the stony tableland soils would post-date the early Recent.

The ancient stony tableland soils are juxtaposed, at the surface of the landscape, with other younger paleosols indicating that the region has had a complex history of soil formation. The survival of paleosols of several different ages is a remarkable feature of the Australian arid zone.

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The writer is indebted to Mr. J. M. Kalmar, C.S.I.R.O., for assistance with field work and for drawing the diagrams, and to Mr. B. E. Butler, Division of Soils, C.S.I.R.O., for helpful suggestions during the preparation of the paper. Fluorescence X-ray spectrography and interpretation of the spectrograms were carried out by Mr. W. Roberts, Bureau of Mineral Resources, Canberra.

REFERENCES

BLACKWELDER, E. 1931. The lowering of playas by deflation. Am. Jour. Sci. 5th ser. **21**, 140–4.

CROCKER, R. L. 1946. The Simpson Desert Expedition 1939. Scientific Reports: No. 8. The soils and vegetation of the Simpson Desert and its borders. Trans. Roy. Soc. S. Aust. **70** (2), 235–58.

CROCKER, R. L. and SKEWES, H. R. 1941. The principal soil and vegetation relationships on Yudnapinna station, north-west South Australia. Ibid. **65** (1), 44–60.

DAVID, T. W. E., and BROWNE, W. R. 1950. The Geology of the Commonwealth of Australia. Edward Arnold & Co., London.

HALLSWORTH, E. G., *et al.* 1951. Desert soil formations in Australia. Aust. Jour. Sci. **13** (4), 110–11.

—— *et al.* 1955. Studies in pedogenesis in New South Wales. VII. The 'gilgai' soils. Jour. Soil Sci. **6** (1), 1–31.

HOWCHIN, W., 1913. The evolution of the physiographical features of South Australia. Rept. A.A.A.S., Melbourne No. 14.

JACKSON, E. A. 1958. A study of the soils and some aspects of the hydrology at Yudnapinna station, South Australia. C.S.I.R.O. Soils and Land Use Series No. 24.

JESSUP, R. W. 1951. The soils, geology and vegetation of north-western South Australia. Trans. Roy. Soc. S. Aust. **74** (2), 189–273.

—— 1960*a*. An introduction to the soils of the south-eastern portion of the Australian arid zone. Jour. Soil Sci. **11**, 92–105.

—— 1960*b*. The lateritic soils of the south-eastern portion of the Australian arid zone. Ibid. **11**, 106–13.

KING, D. 1956. The Quaternary stratigraphic record at Lake Eyre North and the evolution of existing topographic forms. Trans. Roy. Soc. S. Aust. **79**, 93–103.

LEEPER, G. W., *et al.* 1936. Soil and pasture studies in the Mt. Gellibrand area, Western District of Victoria. Proc. Roy. Soc. Vic. **49**, 77–134.

MAWSON, D. 1934. The Munyallina Beds. A late Proterozoic formation. Trans. Roy. Soc. S. Aust. **58**, 187–96.

SPRINGER, M. E. 1958. Desert pavement and vesicular layer of some soils of the desert of the Lahontan Basin, Nevada. Proc. Soil Sci. Soc. Am. **22**, 63–66.

STEPHENS, C. G. 1956. A Manual of Australian Soils. C.S.I.R.O., Melbourne (2nd edition).

(*Received 29 July 1959*)

FIG. 1. Stony tableland soil landscape, Arcoona plateau near Woomera. The stone-covered shelves are practically devoid of vegetation; low shrubs occur in the depressions.

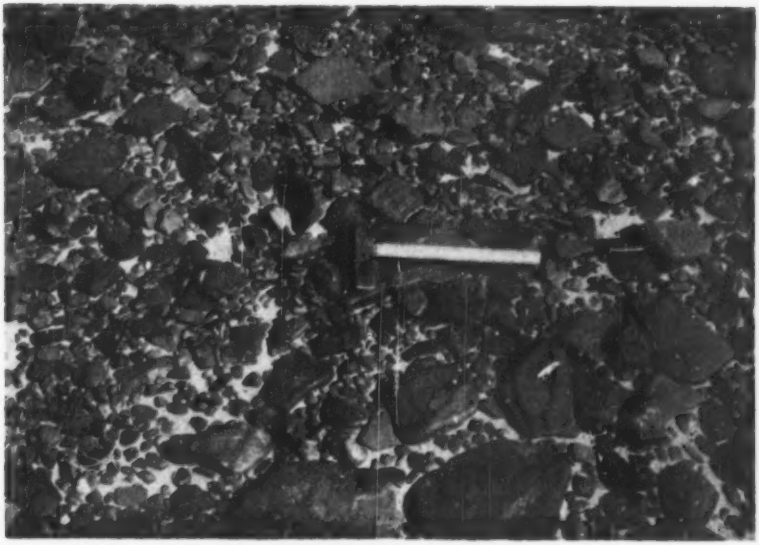

FIG. 2. Shelf stone pavement consisting of sub-angular quartzite showing typical 'desert varnish'. Andamooka, north of Woomera.

R. W. JESSUP—PLATE I

IDENTIFICATION AND SIGNIFICANCE OF BURIED SOILS OF QUATERNARY AGE IN THE SOUTH-EASTERN PORTION OF THE AUSTRALIAN ARID ZONE

R. W. JESSUP

(Commonwealth Scientific and Industrial Research Organization, Canberra, A.C.T.)

Summary

Two soil layers of Quaternary age are identified. The distribution of the layers, the older of which is buried in some areas and exposed in others, is discussed. The soils in each layer are developed on parent materials of predominantly wind-transported origin. The juxtaposition, at the surface of the landscape, of soils with contrasting properties, is interpreted in terms of soil layering and history.

Buried soils indicate that periods of soil formation have alternated with periods of erosion-deposition. The periods of soil formation were associated with relatively humid climates when erosion was at a minimum because the landscape was protected by a well-developed vegetative cover. Each period of soil formation was followed by a period when the climate became increasingly arid and the vegetative cover was depleted. Desertic conditions led to landscape instability and erosion and deposition by wind.

Introduction

A GREAT diversity of soils with a complex distribution pattern has been shown to exist in the south-eastern portion of the arid zone of Australia (Jessup, 1960*a*). Lateritic soils whose formation has been tentatively assigned to the Pliocene, and which were subsequently truncated, are associated with remnants of an ancient land surface (Jessup, 1960*b*). After the formation of the younger land surface above which the lateritic plateaux rise, the stony tableland soil layer, to which a post-early Recent age has been tentatively assigned, was formed (Jessup, 1960*c*).

The two soil layers discussed in the present paper occur in, but are by no means restricted to, erosional incisions in the stony tableland soil layer. They are, therefore, younger than the stony tableland soils. Investigations were carried out in two extensive and representative areas in the south-eastern portion of arid Australia; their location is shown in an earlier paper (Jessup, 1960*a*).

The Soil Layers

An examination of the two regions by means of boring, digging of pits, and inspection of erosion gullies reveals the presence, in some areas, of three different superimposed layers of material overlying the country rocks or truncated lateritic soil.[1]

As will be demonstrated below, the uppermost layer, which shows considerable variation in thickness, consists of sediments in which horizontal or current-bedding is visible. This layer is separated by a

[1] The stony tableland soils are generally not buried beneath these three layers; the reasons for this will be discussed in a following paper.

very sharp boundary from another which varies in thickness up to a maximum of 3 ft. This second layer gradually becomes finer-textured at depth and is highly calcareous throughout; the carbonate occurs in the fine earth and amorphous carbonate may occur in pockets but there are no carbonate nodules.

Below this, and separated from it by a sharp boundary, is a third layer which exhibits well-marked changes in clay and carbonate contents with increasing depth. This lowest layer varies in thickness up to a maximum of 7 ft., and is a non-calcareous loamy sand to sandy loam in its upper portion below which texture gradually changes to sandy clay. The latter contains large amounts of carbonate in the fine earth, in pockets (in an amorphous form) and, in addition, there are carbonate nodules.

The following is a description of a vertical section through the layers at a site east of Wilcannia (sequence 1):

0–2 in. Deposit showing current-bedding due to the presence of alternating very thin ($\frac{1}{16}$ in.) sheets of finer and coarser particles. Texture of layer as a whole is loamy sand; colour is 5 YR 4/8. Separated by a very sharp boundary from:

2–11 in. Apedal[1] sandy loam, 5 YR 5/6 in colour. Soft consistence in dry state, non-sticky and non-plastic when wet. There is a violent reaction with acid, indicating a large amount of carbonate in the fine earth. There is a diffuse boundary with:

11–24 in. Apedal sandy clay loam, 5 YR 5/6 in colour. Slightly hard consistence in dry state, non-sticky and slightly plastic when wet. There is a violent reaction with acid, indicating a large amount of carbonate in the fine earth. Pockets of amorphous carbonate are also present. Sharp boundary with:

24–30 in. Apedal sandy loam, 2·5 YR 4/6 in colour. Soft consistence in dry state, non-sticky and non-plastic when wet. In contrast to the overlying material it is non-calcareous. There is a diffuse boundary with:

30–39 in. Apedal sandy clay loam to sandy clay, 2·5 YR 4/8 in colour. Slightly hard to hard in dry state, slightly sticky and slightly plastic when wet. The material is non-calcareous. There is a diffuse boundary with:

39–72 in. Apedal sandy clay, 2·5 YR 4/6 in colour. Hard in dry state, slightly plastic and slightly sticky when wet. Contains abundant pockets of amorphous carbonate and some carbonate nodules; the presence of carbonate in the fine earth is indicated by a violent reaction with acid.

The superficial layer (0–2 in.) with horizontal or current-bedding consists of contemporary wind-deposited materials (see Jessup, 1960*a*). It is interpreted that the second layer of material (2–24 in.) is a layer of soil. The profile shows weak differentiation; there is a slight rise in clay content, and a change in consistence, with depth. Formation of the profile involved only slight movement of carbonate. The soil in this layer has properties similar to the grey-brown and red calcareous desert soils as defined by Stephens (1956).

[1] The term apedal is used for soil that is structureless; its use avoids the contradiction of stating that the structure of a given soil is 'structureless' (see Butler, 1955, Jour. Aust. Inst. Agric. Sci.). All consistence terms in this paper follow the method of consistence description presented in the U.S.D.A. Soil Survey Manual, 1951. Munsell colour notations are for dry soil.

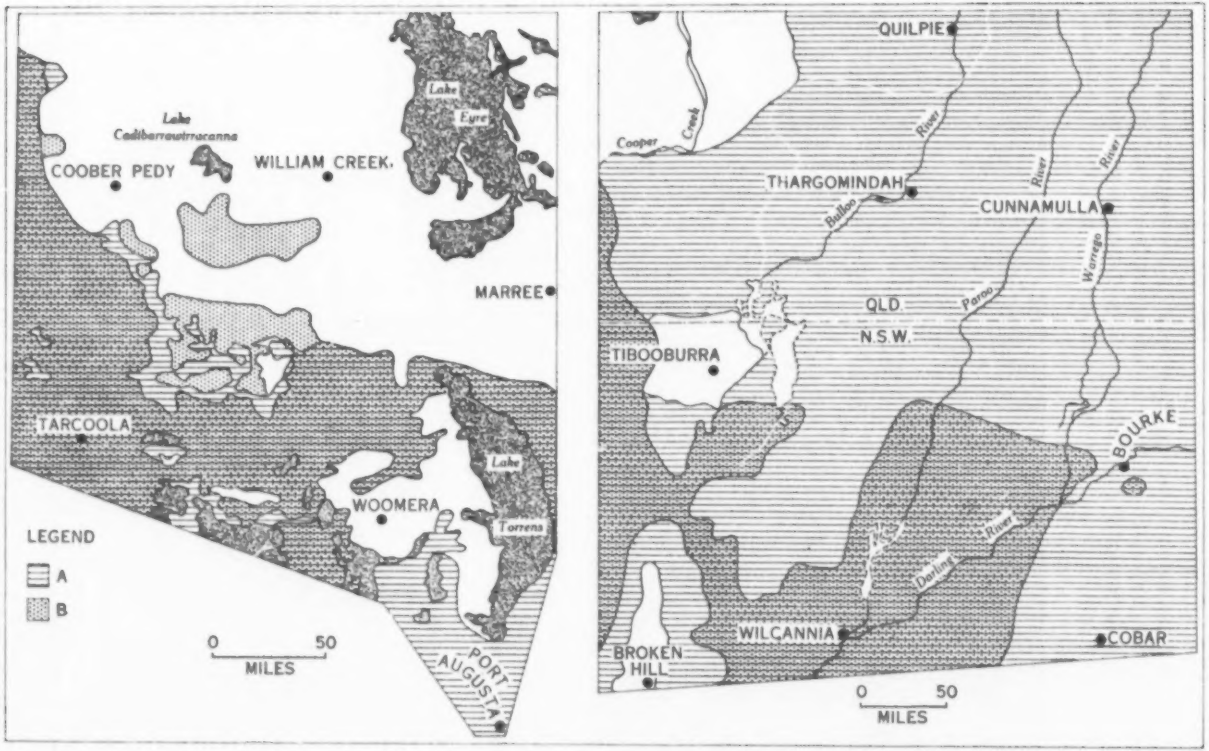

FIG. 1. Showing the distributions of the Bookaloo and Parakylia soil layers in the two areas studied. A, Parakylia; B, Bookaloo.

This soil is separated by a sharp boundary from one in which there is a well-developed carbonate and clay profile (depth 24–72 in.). A, B_1, and B_{ca} horizons occur. During the formation of this lower soil which has the characteristics of a mallisol as defined by Northcote (1956) there was considerable movement of carbonate as is shown by its absence from the A horizon and its presence in pockets and nodules in the B_{ca} horizon.

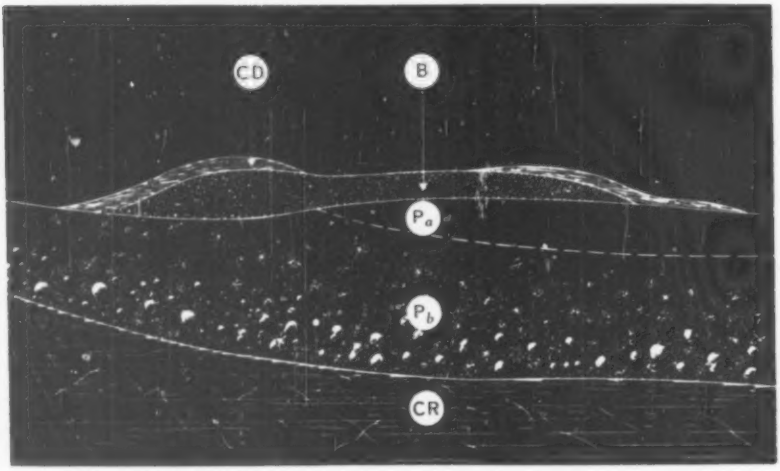

FIG. 2. Diagram illustrating soil layering. CD, contemporary deposits with current-bedding; B, Bookaloo soil layer with carbonate in fine earth throughout profile; P, Parakylia soil layer (P_a is A horizon, leached of carbonate; P_b is B horizon, non-calcareous in upper part but with carbonate in fine earth, pockets of amphorous carbonate and carbonate nodules, at depth); CR, country rock.

These two soil layers always occur in the same stratigraphic order. The names Parakylia and Bookaloo will be used in the following discussion for the lower (older) and upper (younger) layer respectively. The Bookaloo is the youngest soil layer that occurs in the regions studied.

The presence, one above the other, of the layers of soil would require that the upper layer formed on a separate depositional body which was deposited *after* the soil in the lower layer had developed. The soil in the Bookaloo layer was also obviously formed before it was buried beneath the layer of recently-deposited sediments. Thus the presence of buried soils indicates that periods of soil-formation have alternated with periods of erosion-deposition.

The separate identity of the two soil layers is confirmed by the fact that each layer may occur independently of the other. In addition to overlying the Parakylia layer, the Bookaloo layer may directly overlie the truncated lateritic soil or a variety of rocks. The Parakylia layer, too, is found in areas where the Bookaloo layer is absent (Fig. 1[1]) and here the

[1] In a later paper it will be shown that soils other than mallisols also occur in the Parakylia layer.

former may be directly overlaid by the layer of recently-deposited sediments.

The two soil layers occur on all elements in the landscape, including the youngest land surface and ancient land surface residuals (plateaux). Formation of the layers, therefore, post-dated the evolution of the present landscape.

Because the soils in each of the layers have different properties, even when only one layer is present it can be identified as either Bookaloo or Parakylia. Alternatively a single layer can be named by tracing it in the horizontal plane until a situation is reached in which it is overlaid or underlain by the other layer.

When the Parakylia layer is traced laterally it is frequently found that there are situations in which the upper portion of the profile is missing, and that the Bookaloo layer rests, for example, on the B_{ca} horizon of the mallisol (Fig. 2). This indicates that truncation (erosion) occurred before the depositional body, on which the Bookaloo soil subsequently developed, was laid down. Actually truncated buried profiles, not entire ones, are normally found.

Where erosion was severe only the resistant carbonate nodules present in the original Parakylia soil may remain. This is illustrated by the following sequence (sequence 2) near Wilcannia:

0–3½ in. Apedal sandy loam, 5 YR 6/6 in colour. There is a violent reaction with acid indicating a large amount of carbonate in the fine earth. Soft consistence when dry, non-sticky and non-plastic when wet. Separated by a diffuse boundary from:

3½–7 in. Apedal sandy clay loam, 5 YR 7/6 in colour. There is a violent reaction with acid indicating a large amount of carbonate in the fine earth. Soft consistence when dry, non-sticky and slightly plastic when wet.

7–9 in. An accumulation of carbonate nodules, with a trace of soil similar to the above between them. This rests on a non-calcareous sandstone.

Only one layer of soil occurs in this sequence: the soil properties are such that it can be identified as the Bookaloo layer. As indicated above, the soil in this layer contains a large amount of carbonate in the fine earth but it never contains carbonate nodules; the nodules that underlie it must, therefore, be a residue from the Parakylia layer.

The Bookaloo layer has a very extensive distribution (Fig. 1). However, it is not continuous throughout the whole of this area but occurs sporadically; where it is absent, either entire or truncated Parakylia soils are exposed (Fig. 2).

In the more arid areas, even in the absence of man's activities, the soils exposed at the surface are currently being eroded by wind; the materials in the deposit that overlies the Bookaloo soil layer in sequence 1 were derived from adjacent eroding soils.

The Parent Materials of the Soils

In sequence 1 it is evident that the Bookaloo soil must have developed on calcareous parent materials that were deposited on the non-calcareous A horizon of the Parakylia soil. In fact the materials on which the soils

in both layers developed had a transported origin. Thus the calcareous Parakylia soil overlies exposed pallid zone of the ancient lateritic soil, silcrete that caps the lateritic plateaux (Jessup, 1960*b*) and a variety of other non-calcareous rocks such as quartzites and sandstones. The Bookaloo layer may also directly overlie these substrates. The presence of clay in the profiles where the underlying rocks are non-argillaceous is further proof that the soils developed on parent materials of extraneous origin.

Furthermore, in the zones in which they occur the soil layers overlie non-calcareous and non-argillaceous subtrates on hilltops and plateau remnants, that is, they cover the entire landscape irrespective of relief. It is concluded that wind transportation and deposition played a major role in the formation of the parent material layers on which the soils subsequently developed.[1]

However, the parent materials were not, in all areas, transported solely by wind as is indicated by the presence of gravel and stones in some of the profiles. Furthermore, in some areas water-transported deposits were laid down before the accession of the calcareous wind-deposited materials. For example, 13 miles north of Broken Hill there is an erosion gully in which the fine-textured B_{ca} horizon of a Parakylia mallisol is underlain by, and merges with, a non-calcareous fluviatile deposit a few feet in thickness consisting of thin beds of sand, grit, and clay.

Significance of Buried Soils

The presence of buried soils indicates that periods of soil formation have alternated with periods of erosion and deposition. As soil formation takes time (Jenny, 1941), periods of soil formation would require a comparatively stable condition of the landscape with respect to erosion-deposition (Frye, 1951; Butler, 1959). The change from a period of soil formation to one of soil erosion and burial would result from an increase in the rate of erosion-deposition relative to that of soil development.

Wind was the principal eroding and transporting agency involved in the formation of the depositional layers on which the two Quaternary layers of soil formed.

Widespread erosion by wind is, at the present time, everywhere restricted to areas where the surface of the landscape is inadequately protected by vegetation, that is, semi-arid areas where the vegetation has been depleted as a result of man's activities, deserts or periglacial areas; it can safely be assumed that this was also the position in the past.

The recurring periods of erosion involved in the formation of the Quaternary soil layers cannot have been due to the activities of man; Australian aborigines were few in number and neither cultivated the soil nor kept domesticated animals (Elkin, 1948). Furthermore, there was no glacial activity during the Quaternary in the interior of Australia.

Each of the erosional periods must, therefore, have been due to a climatic change involving increasing aridity and leading finally to

[1] The soil layers associated with riverine deposits, such as those in the floodplains of the Darling, Paroo, Warrego, and Bulloo Rivers, have not been investigated.

desertic conditions. The increase in the rate of erosion would have been due to the sparser nature of the vegetative cover. Similar inter-relationships between earlier periods of erosion, aridity, and depletion of vegetation have been discussed by Crocker and Wood (1947), Pitot (1954), and Quinn (1957).

The climates of the soil-forming periods were relatively humid; this is shown by the fact that varying degrees of leaching were involved in the formation of the soils. These relatively humid climatic conditions would have favoured a well-developed vegetative cover, similar to that in humid areas at the present time. It is generally accepted by soil conservationists that a well-developed vegetative cover reduces erosion to a minimum; as indicated above, landscape stability is a prerequisite for the development of soils on newly-deposited sediments.

Butler (1959) has given the name K-cycle to the cycle of stable and unstable periods involved in the formation of layers of buried soils.

Burial of a soil beneath deep deposits terminates its development, since it is no longer exposed to soil-forming processes. It follows that the soils in any one buried layer are all of the same age in the sense that they formed following the deposition of their parent material layer and prior to burial. A soil that was buried during the erosional period of the following cycle formed under the influence of, and was affected by, a single climatic régime; unburied soils of the same age would have been affected by the climates of the stable and unstable periods of each of the ensuing cycles.

Erosion by wind of the soils in the Bookaloo layer and, where it is exposed at the surface, the Parakylia layer now occurs even in the absence of man's activities, that is, the unstable phase of a new cycle has been initiated. The soils in the Bookaloo layer, as well as the Parakylia layer are, therefore, relic.

Because the soils in the two layers have been truncated to varying extents, and both the Bookaloo soil layer and the layer of contemporary deposits are discontinuous, there is a complex soil pattern in both the vertical and horizontal planes. The random soil juxtapositions at the surface of the landscape are the result of an alternating history of erosion-deposition and soil-formation.

Discussion

In areas where the present climate is desertic the soils in the Bookaloo and Parakylia layers are being eroded by wind; the wind-transported materials so derived are deposited in adjacent situations where they frequently bury truncated profiles. As desertic conditions also prevailed when the wind-transported parent materials of the Bookaloo soils were deposited and these deposits accumulated in areas where the soils in the underlying Parakylia layer were frequently truncated (eroded), it seems reasonable to assume that the materials in the deposits were actually derived through erosion of soils in the Parakylia layer.

In a later paper it will be shown that the calcareous wind-borne materials on which the Parakylia soils developed were transported into the areas studied from an extraneous source.

There was some water erosion and deposition during each erosional period prior to the accumulation of the wind-deposited materials. This early phase of water erosion is attributed to the fact that during the earlier stages of the swing towards aridity intermittent rains of high intensity were falling on a landscape partially depleted of vegetation. These periods of water erosion cannot have been due to orogeny as the south-eastern portion of arid Australia had a quiescent orogenic history throughout the Quaternary (David and Browne, 1950). Furthermore, the distribution of the fluviatile deposits bears no relationship to the orogenic patterns of the country, as will be shown in a later paper.

It is, in fact, worth while to consider whether orogeny alone necessarily initiates marked water erosion. Tectonic movements are a prerequisite for water erosion since they provide the necessary relief, that is, erosive potential is increased as a result of orogeny. However, the presence of deep soil mantles on steep slopes protected by a well-developed vegetative cover (see Thornbury, 1954, p. 55) indicates that uplift, *per se*, need not lead to an increase in the rate of erosion even relative to soil-formation. Barrel (1908) has pointed out that the deposition of terrestrial deposits should not be interpreted as being due solely to orogeny since 'climatic changes have at least entered as important contributory factors'.

Climatic change leading to first water, then wind, erosion, and deposition also occurred during the formation of layers of buried soils in the Griffith–Yenda area of New South Wales (van Dijk, 1958).

Jessup (1960*a*) pointed out that no satisfactory explanation had previously been presented to account for the random juxtaposition at the surface of the landscape of the grey-brown and red calcareous desert soils whose genesis involved little movement of clay and carbonate and of mallisols which have well-developed A, B_1, and B_{ca} horizons. The present study has shown that these soils belong to different soil layers, that is, they are of different age and formed under the influence of different climatic régimes; they are both exposed at the surface because the younger layer is discontinuous.

Acknowledgements

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REFERENCES

Barrel, J. 1908. Relations between climate and terrestrial deposits. Pt. I. Relations of sediments to regions of erosion. J. Geol. **16**, 159–90.

Butler, B. E. 1959. Periodic phenomena in landscapes as a basis for soil studies. C.S.I.R.O. Soil Publ. No. 14.

Crocker, R. L., and Wood, J. G. 1947. Some historical influences on the development of the South Australian vegetation communities and their bearing on concepts and classification in ecology. Trans. Roy. Soc. S. Aust. **71**, 91–136.

David, T. W. E., and Browne, W. R. 1950. The Geology of the Commonwealth of Australia. Edward Arnold, London.

Elkin, A. P. 1948. The Australian Aborigines. Angus and Robertson, Sydney.

FRYE, J. C. 1951. Soil-forming intervals evidenced in the Kansas Pleistocene. Soil Sci. **71** (6), 403–8.

JENNY, H. 1941. Factors of Soil Formation. McGraw-Hill, New York.

JESSUP, R. W. 1960*a*. An introduction to the soils of the south-eastern portion of the Australian arid zone. J. Soil Sci. **11**, 92–105.

—— 1960*b*. The lateritic soils of the south-eastern portion of the Australian arid zone. Ibid. **11**, 106–13.

—— 1960*c*. The stony tableland soils of the south-eastern portion of the Australian arid zone and their evolutionary history. Ibid. **11**, 188–96.

NORTHCOTE, K. H. 1956. The solonized brown (Mallee) soil group of south-eastern Australia. VI Congr. Int. Sci. Sol. Rapp. F., 9–19.

PITOT, A. 1954. Vegetation and soils, and their problems in French West Africa. Ann. Éc. Sup. Sci. Dakar.

PRESCOTT, J. A. 1944. A soil map of Australia. C.S.I.R.O. (Aust.) Bull. 177.

QUINN, J. H. 1957. Paired river terraces and Pleistocene glaciation. J. Geol. **65**, 149–66.

STEPHENS, C. G. 1956. A Manual of Australian Soils. C.S.I.R.O., Melbourne.

THORNBURY, W. D. 1954. Principles of Geomorphology. Wiley, New York; Chapman and Hall, London.

VAN DIJK, D. C. 1958. Principles of soil distribution in the Griffith–Yenda district, New South Wales. C.S.I.R.O. Soil Publ. No. 11.

WHITEHOUSE, F. W. 1940. Studies in the late geological history of Queensland. Univ. Qld. Papers, Dept. Geol. **2** (n.s.), No. 1.

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LATERITES AND LATERITIC SOILS IN SOUTH-WESTERN AUSTRALIA

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Summary

A short general account of the distribution and characteristics of the laterites of south-western Australia is given in relation to past and present climates and to climatically controlled processes of landscape development.

A number of erosional and depositional surfaces have been identified near York, Western Australia, the older of which are lateritic, and the characteristics of the laterites and the soils associated with them have been shown to vary with the age of the land surface on which they occur. Extensive sandy deposits derived by the weathering and stripping of the ferruginous horizons of the laterites have been recognized. It is suggested that the 'sand plains' of Western Australia, hitherto considered to be intact or only slightly modified fossil laterites, originated in this way.

Introduction

THE Western Australian laterites, with their hard ironstone crust, over mottled and pallid zones, have been described by Walther (1915) and are generally considered to be fossil soils formed under peneplain conditions during the Tertiary Epoch (Prescott and Pendleton, 1952; Woolnough, 1927). Subsequent epeirogenic uplift has led to the rejuvenation of the river systems, and dissection of the lateritic peneplain or 'old plateau' of Western Australia (Jutson, 1950). According to Stephens (1946) this has resulted in the formation of a younger land surface on which soils have developed which reflect the climatic conditions of the present day. However, a sequence of erosional and depositional surfaces extending in age from the Tertiary towards the present seems more likely, and the evidence presented in this paper shows that such a sequence does exist in Western Australia. The older surfaces carry lateritic soils, the characteristics of the laterite depending on the age of the surface.

Although the climate of Australia has varied since the Tertiary (Whitehouse, 1940), it is likely that the relative incidence of rainfall has remained much the same as at present. Most of the rain falls during the cool winter months, leading to waterlogging of some soils, and there is a general decrease in precipitation with distance inland (Fig. 1). It is therefore not surprising that the characteristics of the laterites, particularly in the depth of the pallid zone, appear to vary with the rainfall. In the higher rainfall areas (Fig. 1) the pallid zones may be 60 or 80 ft. deep, decreasing to about 10 ft. by the 13-in. isohyet.

Further, the geomorphic processes by which the old plateau is being destroyed also appear to be climatically controlled (Peltier, 1950). In the higher rainfall areas the valleys are sharply incised and relatively juvenile, but only rarely are the lateritic materials completely removed, the

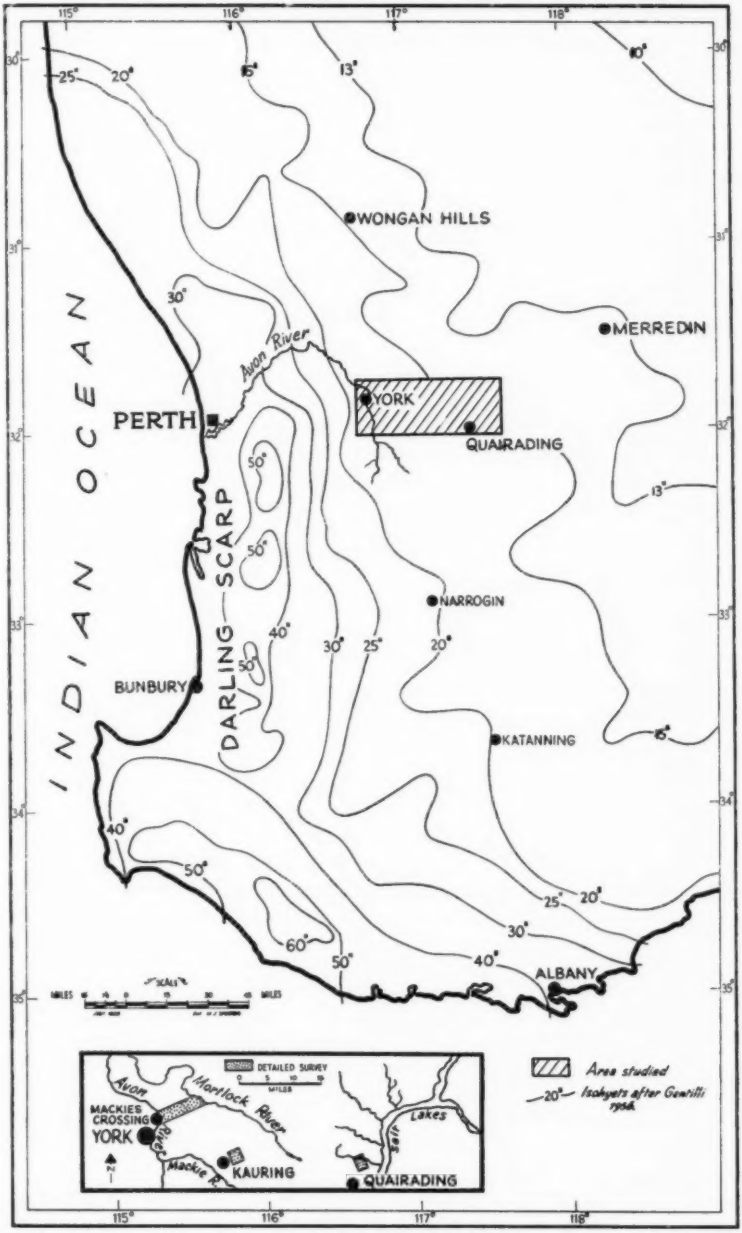

FIG. 1. Locality and rainfall map.

valley sides and floors being clothed with a mantle of lateritic detritus, sometimes re-cemented with secondary iron oxide to form massive pavements at lower levels (Woolnough, 1927; Stephens, 1946). This is particularly the case in situations which are seasonally waterlogged, and the process seems to provide a formidable barrier to further erosion.

Farther inland, roughly in the 20-in. to 15-in. rainfall belt, landscape development has taken place through the retreat of scarps commonly known as 'breakaways', which usually mark the limits of the older, lateritic surfaces, and provide convenient exposures of the laterite profile. The products of erosion are largely, but not entirely, removed from the landscape, thus readily recognizable erosional features are formed, separated by topographic discontinuities. These are the conditions in the area studied (Fig. 1) which will be further considered in the following section.

Beyond this zone, with an annual rainfall of less than 15 in., the rejuvenation of the drainage, consequent on the post-Tertiary uplift, has not affected the valleys to the same extent, so that they are broad and mature. The gently rising interfluves between them carry the 'yellow sand plains' which Teakle (1938) considers to be the 'broken and rounded residuals' of the old plateau. Evidence to be presented here, however, suggests that they are not entirely residuals, but to a considerable degree the colluvially transported products of the destruction of lateritic surfaces by erosion.

Soils and Topography

The area studied is shown in Fig. 1. The country rocks are the Pre-Cambrian granites and gneisses of the Western Australian shield, with occasional intrusions of basic rocks (Wilson, 1958). The latter are comparatively rare and the soils developed on them will not be considered here. The geological structure, with a general north-west – south-east trend, controls the drainage pattern, the main streams being the north-flowing Avon River, a branch of the Mortlock River flowing north-westwards to join the Avon, and the south-west flowing salt lake system east of Quairading. The relief is low, the range of elevation between the valley floors and the old plateau being about 250 ft. over a distance of several miles.

In the course of soil surveys (Fig. 1) it has been established that the pattern of distribution of the soils may be correlated with the occurrence of a number of erosional and depositional surfaces (Mulcahy, 1959), the older of which are lateritic. Of these, the two oldest, named here the Quailing and Kauring surfaces, are together the local expression of the old plateau (Jutson, 1950). It occurs as residuals, often but not always bounded by breakaways, ranging in size from a few square yards to several square miles near the main divides between the Avon and salt lake drainage systems. Both locally and regionally it dips towards the present streams and rivers, indicating that the drainage system as it is today was initiated as long ago as Tertiary times.

The detail of the soils and topography of the old plateau is illustrated

in Fig. 2. The *Quailing erosional* surface occupies the highest parts of the landscape and carries soils of which the following profile is typical:

0–8 in. (P 253.1 and 2)*	A	Yellowish-brown† (10 YR 5/6) sand to sandy loam with very weak crumb structure; some organic staining in the surface 5 in.
8–19 in. (P 253.3)	B	Strong brown (7·5 YR 5/8) sandy clay loam with ironstone gravel. Brittle and vesicular.
19–38 in. (P 253.4)		Strong brown (7·5 YR 5/8) clay loam with dark red (2·5 YR 3/6) mottles and ironstone gravel; brittle and vesicular, continuing.

The profile was described and sampled to a greater depth where exposed in an adjacent breakaway (see also Fig. 4).

0–5 ft. (P 367.1 and 2)	Ferruginous zone	Yellowish-brown hard ironstone becoming slightly softer towards the base.
5–23 ft. (P 367.3–6)	Pallid zone	White and slightly pinkish clay with dark red patches. Quartz grains are bleached in the white clay, stained with iron oxide in the red. Occasional mica flakes throughout. Continuing.
28 ft. (approx.) (P 245.9)	Transitional zone	Pale brown and rusty mottled weathered gneiss.

The ferruginous zone is found as hard, massive ironstone pavements only near breakaways and at the summits of rises (Fig. 2) where exposure is greatest. It has been impossible to make any distinction between ironstone crust and mottled zone, as has been customary (Walther, 1915; Prescott and Pendleton, 1952; Stephens, 1946), as the material of the crust seems to be merely mottled zone hardened when exposed. Occasional inclusions of relatively unweathered rock within the ferruginous zone may be observed in the field enclosed in a coating of iron oxide. Mineralogical studies by Morgan and Herlihy (1956), in association with the author, indicate that the surface yellow sands and the ferruginous horizons generally contain appreciable amounts of easily weatherable minerals, which are absent from the underlying pallid zones though present in the parent rock. Thus it appears that during the formation of the ferruginous zones small pockets of the parent material may be protected from further weathering.

Deep sandy deposits which occur downslope of the Quailing erosional surface form the *Quailing depositional* surface. The soils are sandy yellow earths with relatively undifferentiated profiles consisting of twenty or more feet of yellow-brown sand or loamy sand with slight organic staining in the surface (P 299.1–7). Soft round reddish-brown mottles appear at about 3 ft., which Prider (1946) suggests are ferruginous concretions in the course of formation. The structure of the soils is massive, breaking into irregular soft clods when disturbed. In spite of its sandy nature the

* Numbers in parentheses here and elsewhere in this paper are C.S.I.R.O. Division of Soils sample numbers.

† Munsell colour notation.

material will stand up in a vertical face exposed in a pit, a characteristic in which it resembles the yellow and red earths of eastern Australia. The same assemblage of easily weatherable minerals is present as found in the ferruginous zone of the Quailing laterite and this, with other evidence to be presented later, supports the contention that they are derived from the ferruginous zone by weathering and subsequent colluvial transport.

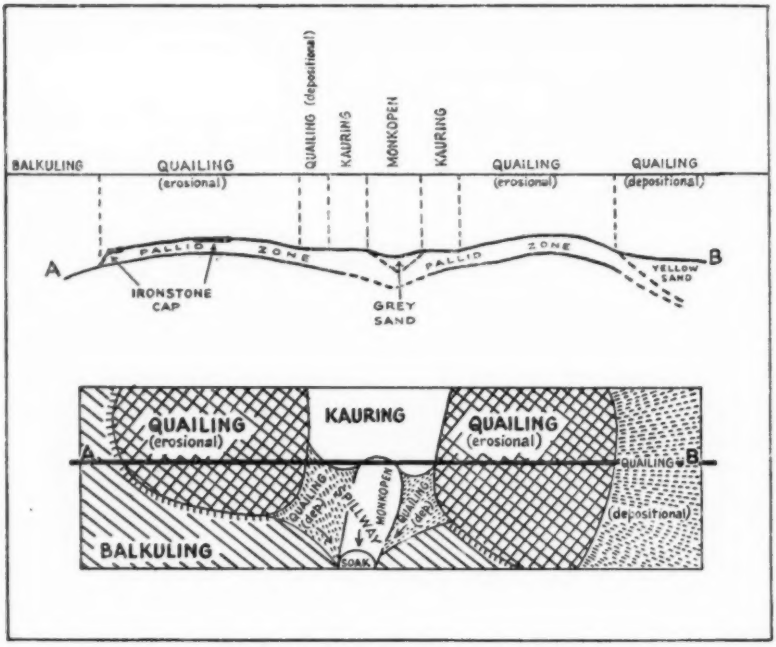

FIG. 2. Detail of the old plateau in plan and cross section.

The *Kauring* surface occupies broad, flat depressions in the Quailing surface. The soil consists of a loose grey sand of variable depth, with some slight organic staining at the surface (P 249.1 and 2), overlying a massive ironstone (P 249.3), paler in colour than that of the Quailing surface, and with occasional inclusions of grey or white weathered rock. Normal pallid zone clays lie beneath. The easily weatherable minerals which are such a feature of the Quailing surfaces are almost entirely absent from the surface grey sand. The profile corresponds with that of the intact laterite described by Northcote (1946), but it is to be noted that it occupies the floors of shallow valleys cut in the Quailing surface, while the inclusions of pallid zone in the ferruginous horizon indicate formation in already weathered material. It may therefore be concluded that the Kauring laterite is younger than the Quailing laterite.

The *Monkopen* surface is formed by a sandy deposit of similar origin to the Quailing depositional material, though probably older, as the

evidence of the soil profile suggests. This consists of 2 or 3 ft. of grey sand (P 247.1–2) similar to that of the Kauring surface, over a pale grey and yellow-brown mottled sandy clay loam (P 247.3) with small round ironstone gravels. This horizon is waterlogged in winter, in contrast to the soils already described which are freely drained throughout. Below, the profile passes into yellowish-brown sand or sandy loam similar to that of the Quailing deposit, which may have a number of bands of ferruginous gravel or hard ironstone at various depths. The Monkopen surface occupies hollows originating at high level in the Kauring surface, and then appears to spill through gaps in the line of breakaways. It is joined *en route* by the yellow sands from the Quailing surface and ends at low level in soaks or springs (Fig. 2) which are valuable sources of good quality water. The two surfaces together form features which have been called 'spillways', and evidence from particle-size studies indicating the transported nature of the materials will be advanced in a later section. Observations from bores and wells show that the deposits vary in depth, tending to be deepest, 50 ft. or more, towards the centres of the spillways (Fig. 2, section AB). They commonly overlie pallid zone material, but other surfaces may be buried by them as well.

The evidence presented up to this stage shows that the laterite of the old plateau has formed in at least two stages represented by the Quailing and Kauring laterites. It has undergone considerable modification by mass wasting (Davis, 1899) since its formation, as shown by the presence of the spillway deposits, which have not been carried out of the system. The youngest of these, the Quailing deposits, show very little in the way of profile differentiation so that their deposition, and hence the stripping of the Quailing laterite, must have continued up to comparatively recent times.

The rejuvenation of the drainage which has taken place in response to the post-Tertiary uplift has, at the same time, resulted in a number of erosional cycles working headwards and in succession along the river systems. Three of these major cycles have been recognized in the area studied, and are represented in Figs. 3 and 4 and the accompanying sections. The surfaces associated with the younger cycles are, of course, extending at the expense of the older, so that only remnants of the latter may be expected.

The oldest cycle is represented by the *Belmunging* and *Mortlock* surfaces, the remnants of the sides and floors respectively, of valleys cut in the old plateau. Both carry lateritic soils. In the case of the Belmunging surface the following is a representative profile description:

0–6 in. (P 302.1)	A	Pale brown (10 YR 6/3) sand with ironstone gravel, loose, structureless.
6–12 in. (P 302.2)	B_1	Light yellowish-brown (10 YR 6/4) loamy sand with ironstone gravel, loose.
12–21 in. (P 302.3)	B_2	Pale brown (10 YR 6/3) and dark reddish-brown (2·5 YR 4/4) mottled sandy loam, compact and hard when dry, brittle.

The Belmunging laterite usually has no pallid zone, except at the lower limits of the slope, the yellowish and reddish mottled ferruginous zone

passing first into reddish-brown clays, and finally country rock at about 12 ft. The B_1 and the top of the B_2 are waterlogged in winter. The latter is soft when wet but hardens irreversibly when exposed in ditches and cuttings. The Belmunging residuals are now found as ridges and spurs

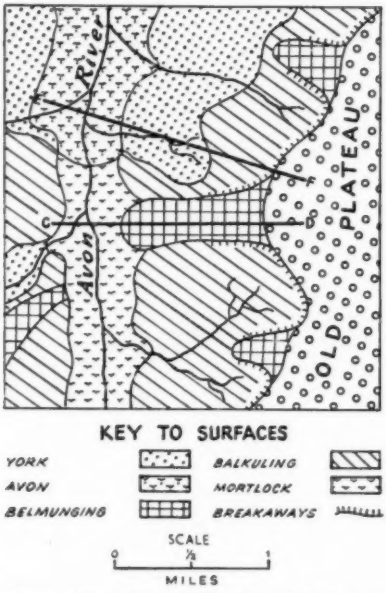

FIG. 3. The dissection of the old plateau.

sloping from the old plateau down towards the drainage lines, often flanked by deep yellow sandy soils similar to those of the Quailing deposits. Where well preserved the spurs end below at the flat terrace-like feature forming the Mortlock surface (Figs. 3 and 4). Here the profile resembles that of the Belmunging soil, though duller colours predominate, and there is longer and more intense waterlogging in winter. The profile does, however, have a pallid zone consisting of kaolinized coarse sediments, often showing the stratification and sorting of a water-laid deposit. The profile may be described as follows:

0–5 in. (P 303.1)	A	Greyish-brown (2·5 Y 5/2) loamy sand, loose, single grain structure, ironstone gravels frequent, with grey coatings.
5–13 in. (P 303.2)	B	Reddish-brown (2·5 YR 5/4) and yellow-brown (10 YR 5/6) mottled sandy clay, compact, slight platey structure. Ironstone gravels abundant, often soft.
13–23 in. (P 303.3)		Laminated light grey (2·5 Y 7/2) yellow-brown (10 YR 5/6) and reddish-brown (2·5 YR 4/4) sandy loam, platey and indurated, continuing.

The *Balkuling* surface is a pediment (Bryan, 1923), growing headward by the retreat of the scarps or breakaways which bound the old plateau and the Belmunging surface (Figs. 3 and 4) and hence it must be younger than both of them. King (1949) states that pediments are rock-cut surfaces, but in this case the cut rock is the weathered material of the

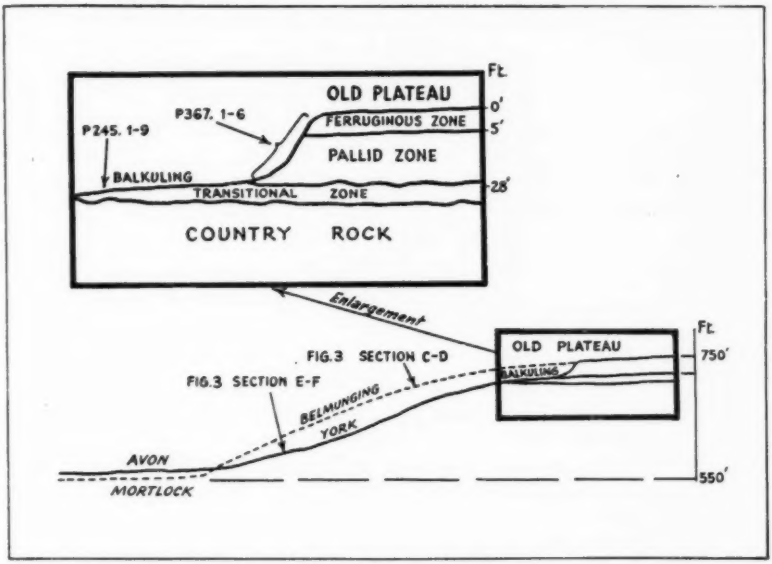

FIG. 4. The laterite profile and its relation to the younger surfaces.

transitional and pallid zones which may be seen outcropping upon the surface. The soils consist essentially of grey or pale reddish-brown clays with a superficial gritty and sandy wash or pedisediment (Ruhe, 1956), decreasing in thickness down the slope. The grey clays are restricted in area, occurring only close to the breakaways bounding the old plateau, and there is no doubt that they are the exposed pallid zone material. The reddish clays developed on the weathered rock of the transitional zone (P 245.9) are far more extensive. The soils usually have no lime in the profile over most of the area, but calcareous profiles become quite common towards the eastern drier end. The following descriptions indicate the range of conditions found:

(*a*) *Non-calcareous profile*

0–2½ in. (P 245.1)	A	Brown (7·5 YR 4/2) sandy loam, crumb structure, loose and friable.
2½–22 in. (P 245.2–4)	B	Reddish-brown (2·5 YR 4/4) and yellowish-red (5 YR 4/6) mottled sandy clay loam to clay, massive, tending to prismatic structure, hard above, becoming more friable below.
22–42 in.		As above, but with fragments of weathered rock.

(*b*) *Calcareous profile*

0–7 in. (P 372.1–2)	A	Dark grey (10 YR 4/1) gritty clay loam, crumb structured and friable.
7–14 in. (P 372.3)	B_1	Greyish-brown (10 YR 5/2) clay, cloddy and massive.
14–28 in. (P 372.4–6)	B_2	As above, but nutty and friable, moderate amounts of free lime in soft concretions.
28–34 in. (P 372.7)		Light brownish-grey clay, compact and massive, lime absent, fragments of pale coloured weathered rock.

The soils are seldom waterlogged even in winter. The surface soil tends to develop a seal, probably due to the impact of raindrops (McIntyre, 1958), which would prevent penetration, and King (1953) points out that pediments in general have a conformation ideally suited to the rapid shedding of large amounts of water. Where, however, the Balkuling surface adjoins a spillway (Fig. 2) it may be overlain by a foot or so of the Quailing or Monkopen deposits. These act as a sand mulch, retaining water so that a water table perches at the buried clay surface. In such situations greyish and rusty mottlings develop in the buried Balkuling surface.

Below, the lower limit of the Balkuling surface is marked by a slight increase in slope (Fig. 4) which is also the upper limit of the youngest cycle of erosion recognized, that represented by the York and Avon surfaces. The *York* surface is characterized by occasional outcrops of fresh rock, the granites and gneisses which form the parent materials of the soils. The dominant soils, though often non-calcareous, have been described as red-brown earths by Prescott (1952) and Teakle (1938). The profile is as follows:

0–7 in. (P 244.1–2)	A	Dark reddish-brown (5 YR 3/3) sandy loam, cloddy, breaking to soft crumbs.
7–30 in. (P 244.3–5)	B	Dark reddish-brown (5 YR 3/4) clay loam to clay, friable with slightly platey structure.
30–36 in. (P 244.6)		Brown clay (7·5 YR 4/4) with slight yellowish-red (5 YR 4/4) mottles: massive, fragments of fresh rock.

The depositional material of the valley floors associated with the York surface has been called the *Avon* surface. The soils are commonly fine textured and calcareous and correspond to the solonized brown and solonized grey soils described by Teakle (1938). The following is a profile of a solonized grey soil:

0–2 in. (P 350.1)	A	Greyish-brown (2·5 Y 5/2) sandy loam, brittle, cloddy, tendency to lamination.
2–6 in. (P 350.2)	B_1	Dark greyish-brown (10 YR 4/2) sandy clay loam; blocky; hard when dry, friable when moist.
6–32 in. (P 350.3 and 4)	B_2	Greyish-brown (2·5 Y 5/2) clay, prismatic to nutty structure; lime present as hard concretions up to 2 in. diameter.

32–48 in. (P 350.5)	Greyish-brown sandy clay (2·5 Y 5/2) with slight rusty mottling; only a trace of lime.
48–80 in. (P 350.6 and 7)	Yellowish-brown (10 YR 5/4) sandy clay loam, no lime, some rounded quartz grit and ironstone gravel.

In all the major valleys examined the Avon surface overlies kaolinized coarse water-laid sediments identical with the pallid zone of the Mortlock laterite. Thus the Avon, and hence the York surfaces, are established as being younger than the Mortlock and Belmunging surfaces, and the relationship is shown in Figs. 3 and 4.

The field evidence, then, shows that a good correlation exists between the distribution of the soils and that of the major geomorphic surfaces, for which a relative age sequence can be established.

Laboratory Examination of the Soils

Soil samples were taken from the profiles described, usually from a pit, but in the case of the complete laterite profile, including the pallid and transitional zones, the samples were taken from the face of a breakaway (see Fig. 4, sample nos. P 367.1–6 and 245.9). The results of the following determinations are presented here:

(*a*) Total analyses for certain elements, and X-ray fluorescent spectrography for iron and zirconium on samples from all zones of the Quailing laterite. The less than 2 μ fractions were also subjected to analysis by X-ray diffraction for clay mineralogy.

(*b*) Particle-size analyses on the spillway sands to show their transported nature.

(*c*) Routine chemical analyses (Piper, 1942) on soil profiles from each geomorphic surface.

The laterite profile

The data on the Quailing laterite profile are summarized in Tables 1 and 2. The pH figures are below 7 for all horizons, falling from 6·5 in the ferruginous zone to 4·9 in the pallid zone, but rising again to 6·0 towards the bottom of the latter. The total analyses demonstrate the extremely weathered nature of the materials, including the transitional zone, and the considerable losses of most elements which have taken place. The calcium and potassium figures are low in all horizons, the latter being most affected. Sodium is relatively high and some, though not all of this, can probably be accounted for by the presence of soluble salts, which rise from 0·007 per cent. in the ferruginous zone to 1·39 per cent. in the base of the pallid zone. These figures, for samples taken from the cliff-like face of a breakaway which may well provide an evaporation front, cannot be taken as representing pallid zones generally. They are, however, given here to emphasise the fact that the lateritic materials provide a source of soluble salts; indeed, brackish springs are not uncommon around the base of the breakaways and on the Balkuling surface fringing them.

TABLE 1

Total Analyses of the Quailing Laterite and Parent Material

Sample no.	*Horizon*	pH	Fe %	P %	Zr *p.p.m.*	Ti %	K %	Na %	Ca %
P 367.1	Ferruginous zone	6·5	1·7	0·008	770	0·49	0·08	0·55	< 0·2
P 367.2	Red mottles	5·2	12·3	0·032	..	0·63	0·03	0·49	0·1
	Yellow mottles		3·08	0·011	..	0·47	0·06	1·93	0·2
P 367.3	Pallid zone	5·3	..	..	100	..	..	..	..
4		5·1	0·55	0·003	101	0·10	0·17	1·0	< 0·2
5		4·9	0·38	0·004	187	0·13	0·38	1·2	< 0·2
6		6·0	..	..	8	..	..	..	..
P 245.9	Transition zone	..	13·0	0·017	..	0·04	0·30	0·76	< 0·2
P 367.7	Parent rock (gneiss)	..	2·1	0·015	39	0·01	7·1	0·62	1·6

TABLE 2

Clay Mineralogy of the Laterite Profile

(Less than 2μ fraction)

Horizon	*Sample no.*	*Minerals present in 2μ fraction*	*Amount*
Ferruginous zone	367.1	Kaolinite	Moderate
		Gibbsite	Moderate
		Quartz	Little
		Haematite or Goethite	Very little
	367.2	Kaolinite	Moderate
		Gibbsite	Much
		Quartz	Very little
		Haematite or Goethite	Very little
Pallid zone	367.3	Kaolinite	Much
	367.4	Kaolinite	Much
		Montmorillonite	Very little
		Inhibited Vermiculite	Very little
		Quartz	Very little
	367.5 and 367.6	Kaolinite	Much
		Illite	Little
		Montmorillonite	Very little
		Inhibited Vermiculite	Very little
		Quartz	Very little

The figures for iron, zirconium, and phosphorus from Table 1 are plotted against depth in Fig. 5. There is a pronounced relative concentration of zirconium in the ferruginous zone which, assuming that it is not removed by weathering, indicates a considerable loss of other materials. In the pallid zone the greatest concentration of zirconium was found at 17 ft. Phosphorus, and particularly iron, are concentrated in the ferruginous and transitional zones and well depleted in the pallid zone. However, the ratios of phosphorus and iron to zirconium (Fig. 6) show that there is an absolute loss of the two former elements in all the weathered horizons.

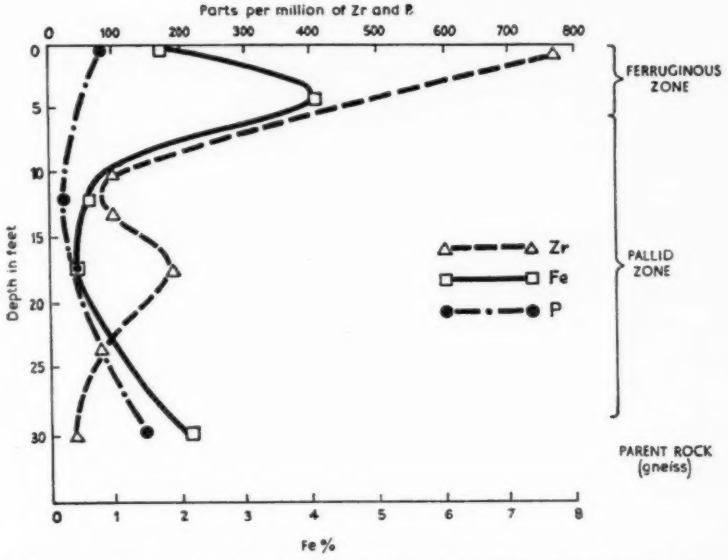

FIG. 5. Zirconium, iron, and phosphorus content of the Quailing Laterite (P 367).

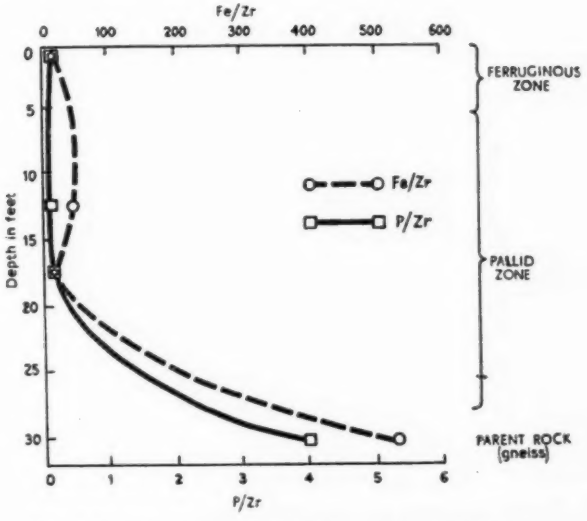

FIG. 6. Ratios of iron and phosphorus to zirconium in the Quailing Laterite (P 367).

The clay mineralogy of the profile shows kaolinite to be the dominant mineral in almost all horizons. The ferruginous zone, with some haematite or goethite, has gibbsite to about the same extent as kaolinite. Gibbsite is absent from the pallid zone, and small amounts of montmorillonite, inhibited vermiculite, and illite appear at the lower levels. The clay mineralogy thus shows that the extreme of weathering is in the surface horizons, decreasing with depth, which is in agreement with the indications from the total analyses.

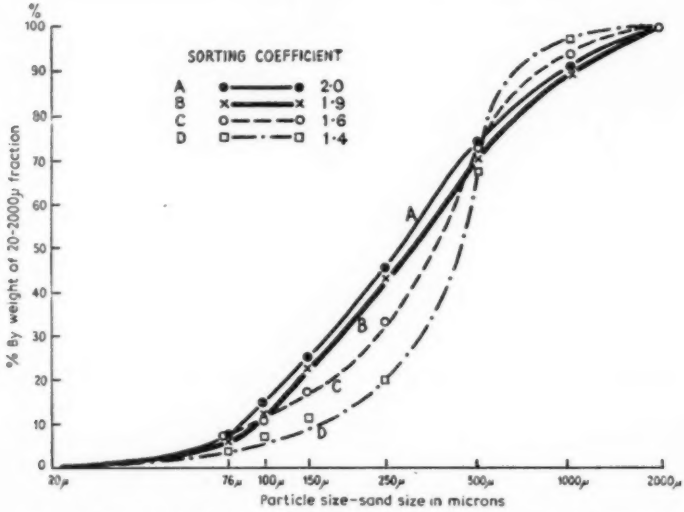

FIG. 7. Changes in particle-size distribution down slope in a spillway.

Particle-size analyses

Special particle-size studies were made on the sandy materials of the spillways in order to establish their transported and depositional nature. Sand fractionation was carried out on the samples after removal of the less than 20 micron fraction by dispersion with 'calgon', and decantation. The 20–2,000 micron material was then fractionated on a set of six standard sieves with apertures of 76, 100, 150, 250, 500, and 1,000 microns by shaking on a gyratory shaker for 20 minutes. Smoothed summation curves for each sample were constructed, plotting the cumulative percentage for each size class against particle size. The sorting coefficient (S_0) of Twenhofel and Tyler (1941) could then be calculated from the expression $S_0 = \sqrt{(Q_3/Q_1)}$, where Q_1 is the particle size at 25 per cent. by weight, and Q_3 that at 75 per cent. by weight.

At a spillway near Mackies Crossing samples were taken at a depth of 6 in. to 12 in. at four sites A, B, C, and D at intervals down a slope, and the summation curves and sorting coefficients at each site are shown in Fig. 7. The decrease in sorting coefficient from A to D shows an increase in degree of sorting with distance travelled.

At another spillway near Kauring the digging of a well to 23 ft. afforded the opportunity to sample the deposit vertically. The deep profile consisted of a foot of greyish-brown sand, with ironstone gravel towards the base, over yellowish-brown sand to sandy loam with a particularly hard band of pisolitic ironstone at 6 to 10 ft. At 23 ft. the yellow deposits rest on pallid zone (P 361.1–11). The results of the particle size analyses are given in Fig. 8. Those for samples in the first 6 ft. were so

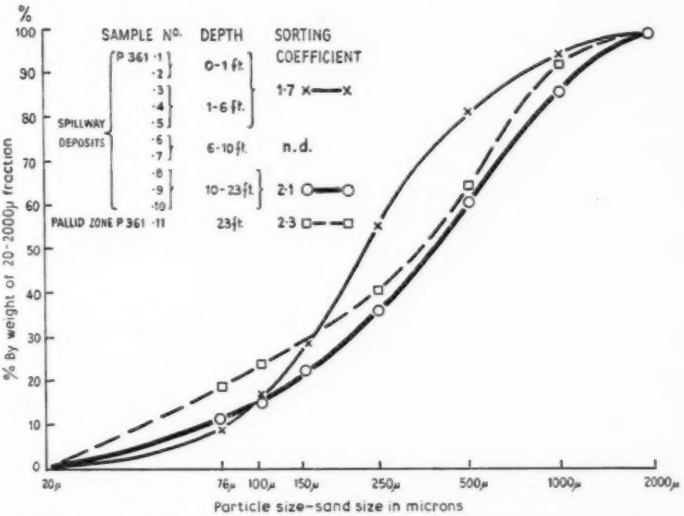

FIG. 8. Change in particle-size distribution with depth in a spillway deposit.

similar that their summation curves almost coincide, as do those from 10 to 23 ft., so that each group of samples is represented here by a single curve. They are separated by a band of hard ironstone (P 361.6 and 7) which was not subjected to analysis. The two curves give sorting coefficients of 1·7 for the upper and 2·1 for the lower material, while the bottom sample, taken from the underlying pallid zone, has a value of 2·3. The figures suggest that there are at least two deposits overlying the pallid zone material. The upper, and therefore younger, deposit is moderately well sorted, while the lower, coarser, deposit has a sorting coefficient only slightly less than that of the weathered gneiss *in situ* beneath it. The intervening hard ironstone may represent a buried soil formed at a time when deposition was halted.

The soil profiles

pH and soluble salts. The soils of the Quailing, Kauring, Monkopen, Belmunging, and Mortlock surfaces are all acid, with pH values ranging from 5·5 to 6·5 and with no free lime in the profile. The total soluble salts seldom rise above 0·01 per cent. in any horizon, with the exception of the profile on the Quailing erosional surface, which has 0·052 per cent.

in the surface rising gradually with depth. The sandy soils of the spillways are, however, notably salt-free (0·004 per cent. total soluble salts), and are extensively used as sources of good-quality water. The Balkuling soils, however, vary in these respects. Though lime-free and acid throughout over most of the area, towards the eastern drier end they tend to become calcareous and high in soluble salts with pH values of more than 8·5 in the subsoils. The soils of the York surface are generally acid in the A horizons, becoming neutral or slightly alkaline with depth. Lime is usually absent but may be present where basic rocks have made some contribution to the parent material. The soluble salts are generally a little higher than in the soils of the lateritic surfaces and spillways. The finer textured soils of the Avon surface, described as solonized brown and grey soils by Teakle (1938), have the highest values for soluble salts which rise to over 0·3 per cent. within 2 ft. of the surface. Calcium carbonate appears in the B_1 or B_2 horizon and the pH rises to over 8·5. Soluble salts remain at about the same concentration with depth, the lime disappears, and the pH returns to the acid side of neutrality.

Exchangeable cations

Data on the subsurface horizons and subsoils of representative profiles from each surface are summarized in Table 3. All are more than 50 per cent. saturated, with the exception of the highly unsaturated grey sand of the Kauring surface, and calcium is the dominant cation, except in the

TABLE 3

Summarized Laboratory Data on the Soil Profiles

Surface	Sample no.	HCl extract P p.p.m.	HCl extract K p.p.m.	Clay %	Exchangeable cations Total m.e./100g	Exchangeable cations Dominant metal ion	Exchangeable cations Saturation %
Quailing (erosional)	P 253.3	33	590	21	6·8	Ca	56
	P 253.4	33	820	25½	..	..	..
Quailing (depositional)	P 299.4	25	< 50	9	2·0	Ca	60
Kauring	P 249.2	13	< 50	3	1·0	Ca-Mg	17
	P 249.3	15	60	4	1·3	Mg	23
Monkopen	P 247.3	18	< 50	9	1·7	Mg	53
	P 247.4	..	..	14	2·9	Ca	52
Belmunging	P 302.2	48	160	10	4·1	Ca	61
	P 302.3	53	390	29	7·1	Mg	55
Mortlock	P 303.2	50	390	28	5·7	Ca-Mg	58
	P 303.3	50	390	17	7·0	Mg	57
Balkuling:							
(a) Non-calcareous	P 245.2	61	160	24	8·6	Ca	52
	P 245.5	36	310	50	8·7	Mg	71
(b) Calcareous	P 372.2	56	1,510	37	20	Ca	100
	P 372.7	46	2,150	..	..	Ca-Mg	100
York	P 244.2	69	1,100	8½	7·2	Ca	67
	P 244.4	..	..	36	11·2	Ca	66
Avon	P 350.2	85	1,640	24	14·4	Ca-Mg	100
	P 350.4	48	2,350	40	13·0	Ca+Mg*	100

* Exchangeable Na 30–40 per cent. of the cations; Ca + Mg 60–70 per cent., not determined separately due to high salt concentration.

seasonally waterlogged subsoils of the Belmunging and Mortlock surfaces, where magnesium exceeds it. Sodium may rise to 30 per cent. or more of the cations in the deeper subsoils of the solonized brown soils and the more saline Balkuling soils. The total exchangeable cations are low, particularly in the sands of the spillways and the Kauring surface.

Phosphorus and potassium

The phosphorus and potassium contents of the hydrochloric acid extracts (Piper, 1942) are shown in Table 3. The sands of the Kauring surface and spillways are strikingly low in both elements. The soils of the Quailing, Belmunging, and Mortlock lateritic surfaces have phosphorus contents approaching those of the red-brown earths and solonized brown soils of the York and Avon surfaces, but they differ considerably in acid soluble potassium content, the laterites having only something of the order of one-fifth to one-quarter the content of the non-lateritic soils. However, the non-calcareous soils of the Balkuling surface, developed on the highly weathered rocks of the transitional zone, have lower potassium figures than some of the laterites.

Discussion

The evidence presented shows the existence of a number of cyclic erosional and depositional surfaces, and indicates their relative ages. No new evidence as to their absolute ages is offered at this stage. However, correlation with the soils and depositional systems of the Swan Coastal Plain near Perth, for which McArthur and Bettenay (1960) have proposed absolute ages, may be possible with further field studies. The surfaces recognized and the soils associated with them display a number of features which are the consequences of their age and genesis.

The oldest laterite, that of the Quailing erosional surface, occupies the highest points in the landscape, and is underlain by the deepest pallid zones. It has been considerably stripped, so that the ferruginous horizon provides the parent material for the relatively poorly developed soils now found on it. In this it contrasts with the younger Kauring laterite, in which a surface horizon of grey sand over the ironstone is still present. The youngest are the Belmunging and Mortlock laterites, formed on the sides and floors of valleys cut in the old plateau. Here the depth of weathering is considerably less than on the older surfaces, a striking feature of the Belmunging being the absence of pallid zone.

The stripping of the Quailing and, to some extent, the Belmunging surfaces must be regarded as the source of the spillway deposits, the transported nature of which is established by the particle-size analyses. Further, the changes in mechanical composition with depth, and the occurrence of bands of ironstone gravel at various depths, suggest that deposition has taken place under different conditions at different times, probably separated by periods of soil formation. The relatively undifferentiated nature of the profile on the Quailing deposits means that the process has continued up to fairly recent times. While the deposits occupy but a relatively small proportion of the landscape in the area studied, in the drier country to the east this form of modification of the old plateau has

been the dominant process of landscape evolution. Vast areas are mantled by considerable depths of Quailing and Monkopen deposits, which form the 'sand plains' of Western Australia. While Prescott (1952) considers the sand plains to be fossil soils *in situ* which have suffered the minimum of denudation, the view advanced here is that they are in large part deposits, derived by the colluvial transport of material provided by the weathering and destruction of the ferruginous horizons of laterites. Resegregation of iron has taken place within the deposits giving hard ironstone bands, which may be re-exposed at the surface by further stripping.

The Balkuling surface carries soils which have as their parent material the transitional zone of the laterite profile exposed by truncation, i.e. they are developed on already weathered material, as shown by the analytical results presented in Table 1. The soils show a marked change in properties with climate, becoming more calcareous and saline as the rainfall decreases with distance eastwards, but this cannot be interpreted as a direct effect on soil development. The analyses of the pallid zone of the Quailing laterite show that it can act as a source of soluble bases, and brackish seepages flowing out of this material exposed in breakaways emerge on to the Balkuling surface. Therefore the rise in lime and salts may well be due to such small secondary accessions over a long period. Beyond the eastern limits of the area studied the Balkuling surface is often well expressed, though it may be mantled with pedisedimentary layers of variable depth, and columnar and domed subsoil clays are not uncommon. The Avon and York surfaces, the youngest recognized, carry red-brown earths and solonized grey or brown soils respectively. These have not been closely studied and it is not proposed to discuss them further here, other than to stress the age relationship with the Mortlock and Belmunging surfaces, illustrated in Fig. 4, where the former overlies the latter, and to emphasize the contrast in properties between them and the soils of the older surfaces.

Thus it appears that laterites may develop not only under peneplain conditions of low relief, but also on valley sides and floors, the former attaining slopes of up to 8° (McWhae, 1945), and also in deposits such as those of the spillways. The occurrence of lateritic materials cannot, therefore, be accepted uncritically as an indication of old peneplain levels, but must be considered in relation to geomorphic evidence before their significance can be assessed. However, as time seems to be the essential factor for the development of lateritic surfaces, a low available relief is necessary, so that erosion is relatively ineffective and land forms may be preserved for long periods, though modified as described in this paper. Once laterite has formed, its presence tends to preserve the form of the landscape due to the induration of the ferruginous zone with exposure, so that such modifications are kept to a minimum. The fact that they have taken place, however, means that the soils are not always as old as the surfaces on which they are found. Even so, there is a marked correlation between the distribution of the soils and that of the major land surfaces. This is in contrast to the conclusions of van Dijk (1959) in eastern Australia, where major land surfaces of different ages carry

essentially the same sequence of soils. In the latter case, in the absence of the zones of deep weathering associated with laterites, minor planations of the surfaces can remove complete soils, exposing fresh parent materials so that soil formation recommences *ab initio*.

The laboratory data demonstrate the considerable losses, particularly of bases, associated with lateritisation, so that the low natural fertility of the soils is not surprising. The sands of the Kauring and Monkopen surfaces are the poorest, closely followed by those of the Quailing deposits, otherwise the values for nitrogen, phosphorus, potassium, and exchange capacities show a general trend increasing from the oldest to the youngest surfaces. Trace element deficiencies, particularly copper and zinc, are commonest on the older and sandier soils, though molybdenum responses seem to be confined to the soils of the younger, non-lateritic surfaces (Teakle, 1944; Fitzpatrick, 1957).

Under the prevailing climatic conditions moisture stress is an important limiting factor on the deeper sands. These soils are also particularly liable to wind erosion, the incidence of which appears to be greatest, not on the higher more exposed sites, but downslope in the spillways where the sands tend to be farther travelled and of smaller particle size. The pediment forming the Balkuling surface constitutes another important erosional hazard. Such surfaces are particularly efficient in the shedding of water by sheet flow (King, 1953; Holmes, 1955) so that sheet erosion may be expected. Disturbance of the natural balance, as for example in clearing for agriculture, may convert sheet to stream flow which can cut deep gullies in a short period. The brackish springs which are common on the Balkuling surface, especially near its junction with the York surface, result in bare areas where erosion is likely due to the absence of plant cover.

Conclusion

A number of erosional and depositional surfaces have been recognized, and the older of these are lateritic. Laterite has been shown to occur not only on peneplain remnants but also on the sides and floors of mature valleys. The low available relief and relative erosional stability over long periods has tended to favour laterite formation, and the ferruginous horizons which indurate on exposure tend to preserve the surfaces on which they have formed. Because of this and the accompanying deep weathering, the minor planations which they have suffered have been ineffective in destroying the soils associated with the residual lateritic surfaces other than removing the leached grey sandy A horizon. Thus there is a marked correspondence between the age of the land surfaces and the kind of soil found on them, and this relationship is useful, both as a tool in mapping the distribution of the soils and as a basis for studying their genesis.

While the pedological results of laterite formation in the segregation of sesquioxides and loss of bases have been particularly stressed in the literature, there is another, secondary effect, which assumes considerable importance under the conditions prevailing in south-western Australia. The development of the grey sandy A horizon is followed by stripping to

expose the ferruginous B horizon which, as has been shown, by further weathering and stripping, can act as a source of deep and extensive sandy deposits. These processes, if repeated over long periods, and if the deposits are not removed from the system, provide a mechanism for the separation and retention of the resistant quartz sands within the landscape, while less resistant primary and secondary minerals are destroyed. This is proposed as the general mode of formation of the Western Australian sand plains.

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REFERENCES

BRYAN, Kirk. 1923. Erosion and sedimentation in the Papago country, Arizona. U.S. Geol. Surv. Bull. **730,** 19–90.

DAVIS, W. M. 1899. The geographical cycle. Geogr. J. **14,** 481–504.

FITZPATRICK, E. N. 1957. Molybdenum for subterranean clover. J. Agric. W. Aust. **6,** 65–68.

GENTILLI, J. 1956. Weather and Climate in Western Australia. Western Australian Government Tourist and Publicity Bureau.

HOLMES, C. D. 1955. Geomorphic development in humid and arid regions: a synthesis. Amer. J. Sci. **253,** 377–90.

JUTSON, J. T. 1950. The physiography of Western Australia. Bull. Geol. Surv. W. Aust. No. 95.

KING, L. C. 1949. The pediment land form: current problems. Geol. Mag. **86,** 245–50.

—— 1953. Canons of landscape evolution. Bull. Geol. Soc. Amer. **64,** 721–32.

MCARTHUR, W. M., and BETTENAY, E. 1960. The development and distribution of the soils of the Swan Coastal Plain, Western Australia. C.S.I.R.O. Aust. Soil Publ. No. 16.

MCINTYRE, D. S. 1958. Permeability of soil crusts formed by raindrop impact. Soil Sci. **85,** 185–9.

MCWHAE, J. R. H. 1945. The geology and physiography of the Lawnswood area. J. Roy. Soc. W. Aust. **32,** 49–74.

MORGAN, K. H., and HERLIHY, J. H. 1956. The geology of the Kauring area. Thesis, Univ. of W. Aust.

MULCAHY, M. J. 1959. Topographic relationships of laterite near York, Western Australia. J. Roy. Soc. W. Aust. **42,** 44–48.

NORTHCOTE, K. H. 1946. A fossil soil from Kangaroo Island, South Australia. Trans. Roy. Soc. S. Aust. **70,** 294–6.

PELTIER, L. C. 1950. The geographic cycle in periglacial regions as it is related to climatic geomorphology. Assoc. Amer. Geogr. Ann. **40,** 214–36.

PIPER, C. S. 1942. Soil and Plant Analysis. University of Adelaide.

PRESCOTT, J. A. 1952. The soils of Australia in relation to vegetation and climate. C.S.I.R. Aust. Bull. No. 52.

—— and PENDLETON, R. L. 1952. Laterite and Lateritic Soils. Commonw. Bur. Soil Sci. Tech. Commun. No. 47.

PRIDER, R. T. 1946. The geology of the Darling Scarp at Ridge Hill. J. Roy. Soc. W. Aust. **32,** 105–29.

RUHE, R. V. 1956. Landscape evolution in the High Ituri, Belgian Congo. I.N.E.A.C. Ser. Sci. No. 66.

STEPHENS, C. G. 1946. Pedogenesis following the dissection of lateritic regions in southern Australia. C.S.I.R. Aust. Bull. No. 206.

TEAKLE, L. J. H. 1938. A regional classification of the soils of Western Australia. J. Roy. Soc. W. Aust. **24,** 123–95.

—— 1944. Molybdenum as a fertiliser in Western Australia. J. Agric. W. Aust. **21,** 335–9.

TWENHOFEL, W. H., and TYLER, S. A. 1941. Methods of Study of Sediments. McGraw-Hill Book Company Inc., New York and London.

VAN DIJK, D. C. 1959. Soil features in relation to erosional history in the vicinity of Canberra. C.S.I.R.O. Aust. Soil Publ. No. 10.

WALTHER, J. 1915. Laterit in West Australien. Z. dtsch. geol. Ges. **67B,** 113–40.

WHITEHOUSE, F. W. 1940. Studies in the late geological history of Queensland. Univ. Qld. Papers Dept. Geol. No. 2.

WILSON, A. F. 1958. Advances in the knowledge of the structure and petrology of the Precambrian rocks of south western Australia. J. Roy. Soc. W. Aust. **41,** 57–83.

WOOLNOUGH, W. A. 1927. The duricrust of Australia. Proc. Roy. Soc. N.S. Wales. **61,** 24–53.

(*Received 8 August 1959*)

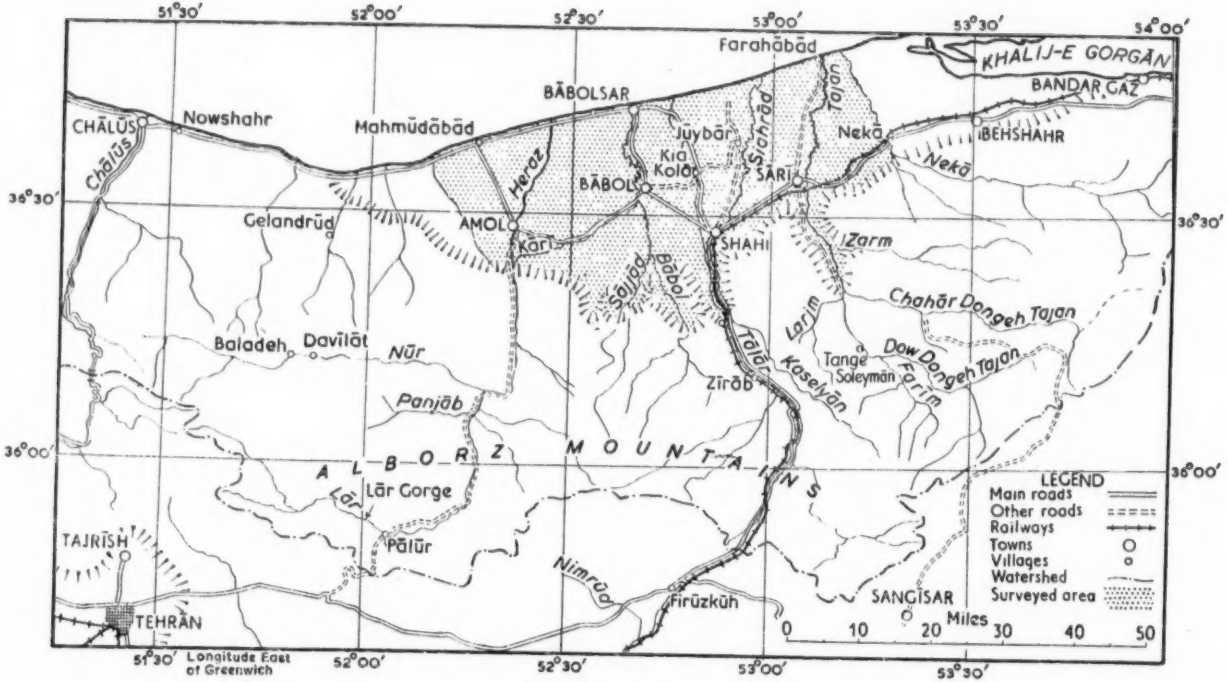

FIG. 1. Situation map.

THE SOILS OF MAZANDERAN IN NORTHERN IRAN AND THEIR SUITABILITY FOR PADDY-RICE IRRIGATION

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Summary

The soils which occur along the southern shore of the Caspian Sea, in the Mazanderan Province, which is one of the main rice-producing regions in Iran, are formed mainly from young alluvial deposits in which pedo-climate is considered to be the major soil-forming factor.

According to differences in pedo-climate, the soils have been differentiated into soil associations which are related to the topographical situation in which they occur, namely the several landscapes characteristic of the morphology of a well-developed riverine plain.

The occurrence of salty soils can be explained by the influence of the Caspian in the past, and their reclamation, although theoretically possible by drainage improvement, the application of soil amendments, and adequate leaching, has been found to be very difficult in practice. Soil analyses have shown interrelationships between natural vegetation or crop yield and salty conditions.

The soils have been further classified according to their suitability for paddy-rice cultivation, particularly with regard to the economy of irrigation water.

As none of the irrigability classifications yet devised appears to be suitable for the purpose of classifying rice soils, a special system has been developed to meet the circumstances prevailing in Mazanderan.

Introduction

In world literature little mention is made of the soils which occur in Northern Iran. Joffe (1949, pp. 245–57) classified them by interpolation as members of the Brown and Chestnut-brown Soil Groups.

It is the object of this paper to give a wider knowledge of these soils and in particular those found in that part of the Mazanderan Province bounded in the south by the steeply rising Alborz Mountains and in the north by the Caspian Sea (Fig. 1).

A semi-detailed soil survey was carried out in the region during 1957 on behalf of the Dam Building and Irrigation Division of the Government of Iran in connexion with the second Seven-year Plan for development. This survey formed part of intensive investigations carried out by a firm of consulting engineers to determine the possibilities of extending traditional paddy-rice growing by more economical use of the available water resources and the storage of water during winter and spring by constructing large dams on the main rivers. For this purpose the soils of the plain were mapped and classified according to their suitability for rice-growing. None of the existing irrigability classifications can be used for the specific purpose of classifying rice soils as they are all based on the needs of dry-foot crops. An irrigability classification was therefore compiled specifically for rice-growing on alluvial soils. This classification could be applied extensively in similar rice-growing areas in the world.

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General Characteristics of the Area

The area surveyed is situated on the plain between the northern slopes of the Alborz Mountains and the Caspian Sea and is about 1,000 square miles in extent.

Physiographically the plain may be divided into seven distinct landscape units (Fig. 2), namely:

1. Three main alluvial fans or cones which have formed at the debouching points of the three main rivers—the Heraz, Talar, and Tajan.
2. Prominent levees along the main rivers together with relics of old levees built up during the formation of the riverine plain.
3. Low-lying basins or bottomlands between the levees.
4. The old lagoon.
5. The off-shore bar which at one time formed the coast-line north of the old lagoon; the off-shore bar is still forming in the east (Fig. 1) outside the surveyed area. In the area itself only remnants of this barrier are found as part of it has been eroded by transgressions of the Caspian in the past ten centuries. Evidence of recession of the coast-line is found as far as 10 miles inland on the plain where areas of salty land once submerged by the sea are found.
6. Recently formed dunes along the coast-line on the northern edge of the plain.
7. Colluvial material derived from the neighbouring hills in the south form the transition between the plain and the foothills of the Alborz Mountains. These regions have been termed *Hillfoot Areas.*

Immediately behind the off-shore bar, and often in the stretch between it and the recent dunes, the soils are partly salty. This has been caused by the accumulation of salts from the sea in the past. Owing to the heavy texture of the soils and the almost flat relief, natural drainage is impeded and the salts have not been leached out. The soils were further enriched by salts through several invasions by the Caspian whereby seawater submerged the lagoon. This subsequently acted as an evaporation pan similar to the Kara-Bougas (H. Kuenen, 1950) but on a smaller scale.

Climate

The climate of Mazanderan is characterized by warm, fairly humid summers and mild, humid winters. The rainfall is greatly influenced by the barrier of the Alborz Mountains which deflects the movements of the air masses from the Caspian Sea and causes precipitation on the northern side of the watershed. On the plain itself the mean annual rainfall is approximately 28 in. The rainfall along the coast apppears to be a little lower than in the southern part of the plain and there is evidence that it also increases in the west. The winters are slightly wetter than the summer seasons but in general the rainfall is well distributed throughout the year.

The mean temperatures in summer and winter are approximately

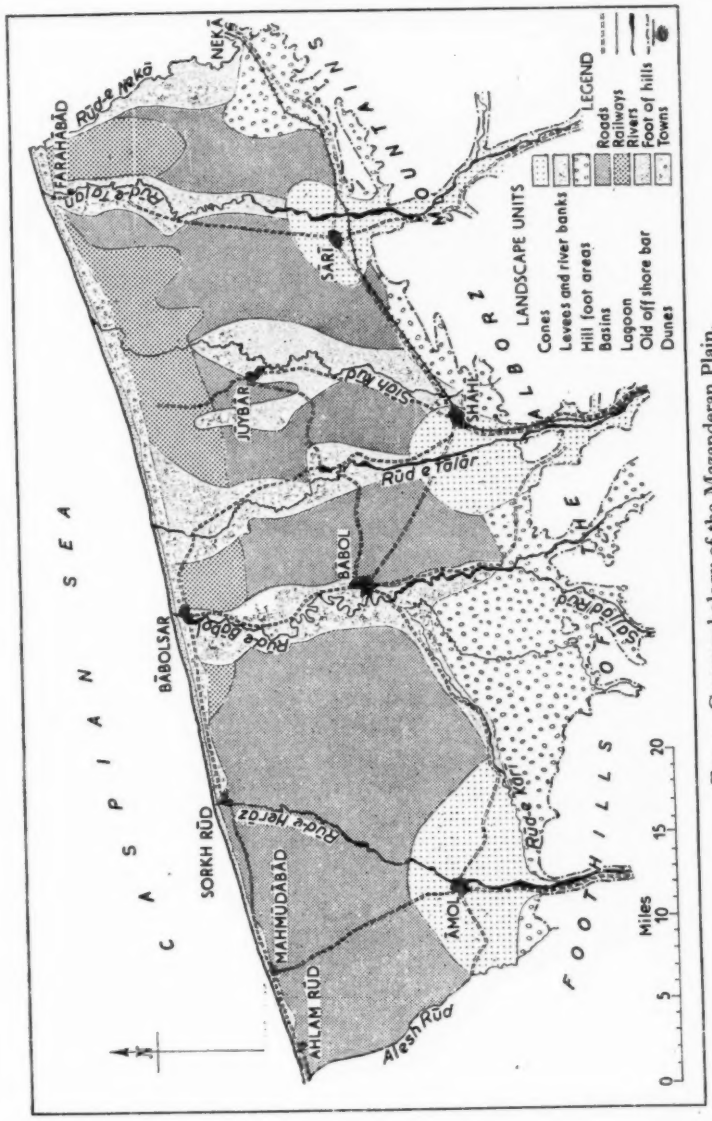

FIG. 2. Geomorphology of the Mazanderan Plain.

78° F. and 44° F. respectively. The temperatures along the coast are always a little lower in summer and higher in winter owing to the close proximity of the Caspian. Frost occurs occasionally in the foothill areas and is very rare along the coast. The mean daily humidity is about 80 per cent. throughout the year.

Vegetation

The natural vegetation in the greater part of the plain has already been removed by man. The typical forest associated with this humid, mild subtropical climate is still existent in other parts of the plain but does not occur in the surveyed area. Natural vegetation occurs in salty areas where crop production is impossible. In these areas the dominant plants are salt-tolerant to varying degrees depending on the salt content of the soils and also the depth and duration of flooding which occurs in the winter.

The most important plants in the salted areas are:

(i) *Cynodon dactylon*: a short grass species, which generally occurs in areas where the salt content of the soil fluctuates owing to periodic leaching during the winter.
(ii) *Juncus acutus*: occurs in areas which are permanently affected by salty conditions.
(iii) *Salicornea* sp.: which indicate severely salty conditions.

The farmers have attempted to cultivate the salty areas by growing rice, wheat, barley, and cotton. Analyses of soil samples taken from these areas have shown that the salt content has definitely been the cause of crop failure and show clear correlations between the salt content of the soil, natural vegetation, and crop yield (Table 1).

TABLE 1

Relation between the Salt Content of the Soil and Natural Vegetation or Minimum Crop Growth

Salt content mmhos/cm. E.C. at 25° C. in satn. extract	*Natural vegetation or minimum crop growth*
>18	*Salicornea* sp.
18	*Juncus acutus*
16	Barley*
15	*Cynodon* sp. (Bermuda grass)
10	Cotton
9	Wheat*
8	Rice*

* Crop only suitable for cattle fodder—uneconomic yields of grain.

Cotton thrives vegetatively at a salt level of 10 mmhos/cm. E.C. but actual yields are very poor. For agricultural purposes a salt level of 6 mmhos/cm. E.C. sets a limit as rice is then the only crop which gives satisfactory yields in spite of the high salt saturation. It fails

however, to produce sufficient grain at a salt level not much higher than 6 mmhos/cm. E.C.

The results of these investigations are well in agreement with the figures given for the relative salt tolerance of crop plants, produced by the United States Salinity Laboratory Staff (1954, p. 67).

Soil Classification

All the soils of the Mazanderan plain are derived from the alluvial materials transported by the three major rivers—the Heraz, Talar, and Tajan. Borehole drilling records indicate that these deposits are possibly more than 6,000 ft. deep and consist of poorly consolidated sands, gravels, and clays of Quaternary and Late Tertiary age. The sources of these materials are in the Alborz Mountains, which are composed of consolidated rocks, chiefly limestones and sandstones of Mesozoic and Early Tertiary age. In the Heraz catchment area there is an admixture of volcanic material derived from Demavand, a cone more than 18,000 ft. in height.

In general atmospheric climate is not the main factor affecting soil formation in Mazanderan. The concept of grouping soils according to climatic zones has been applied by Joffe (1949, pp. 245–57) to the soils of Northern Iran. It is suggested, however, that the nature of the parent materials and the consequent pedo-ecological factors such as drainage and permeability are the most important soil-forming factors in this region.

(i) *Texture*

The geomorphology of a well-developed riverine plain is such that the situation of each physiographic unit in the plain defines the pedo-climate prevailing in that unit. The reasons are that the soil of each physiographical or landscape unit is not only characterized by a typical situation in relief but also by a specific texture. The decreasing velocities of the river waters flowing from the mountains towards the sea cause a natural grading of the deposited materials not only along a line parallel to the streambeds but also in sections at right angles to them (Fig. 3).

The coarsest material is found in the streambeds near the debouching points of the rivers on to the plain. The river-banks being the highest points of the levees are formed by materials varying from sandy loam to silt. The levees in the narrow sense[1] are built up mainly by silt loam to silty clay loam deposits. They show a definite layering in their profiles, the layers dipping slightly towards the basins. Silty clays are deposited in the low-lying areas or basins, while the finest particles, the silty clays to heavy clays, settle in the old lagoon behind the off-shore bar in almost still water.

The cones show a similar succession but in vertical section. The substrata are gravelly with increasingly finer materials deposited on top.

[1] The whole ridge along the streambed is morphologically called 'levee'. For mapping purposes we distinguished 'the river-bank' being the crest of the levee, while the main part of the levee which slopes towards the basin is called 'the levee in the narrow sense'.

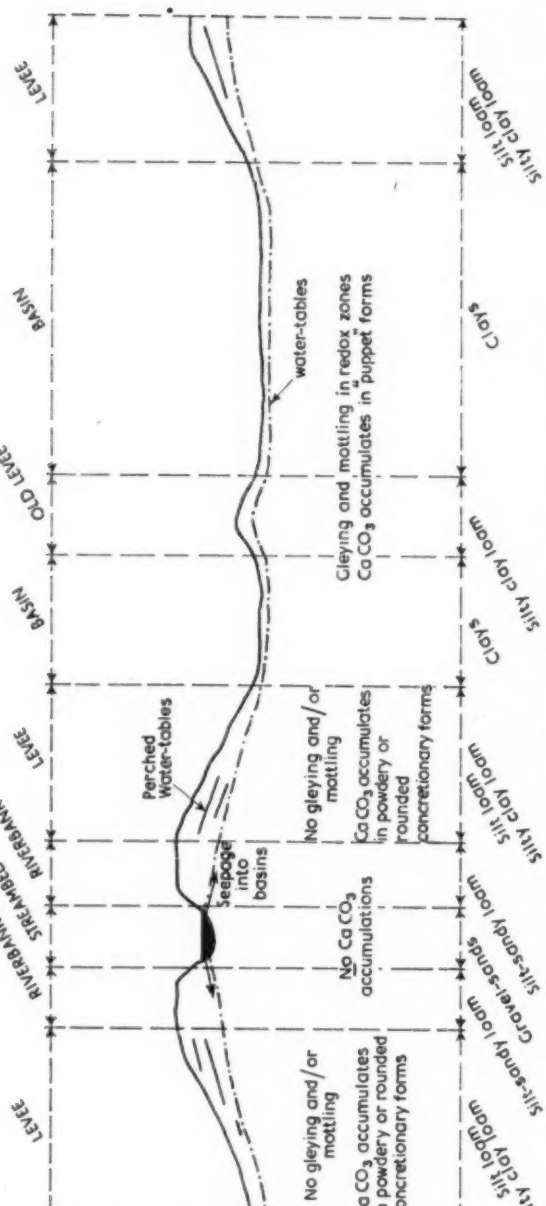

FIG. 3. Cross-section of the depositional system on the Mazanderan plain.

Each landscape unit is therefore defined by a topographical situation and by soils of specific textures. Drainage, permeability, height of water-table, aeration, and leaching are closely related to these two factors.

(ii) *Water-table*

Most of the river-beds lie slightly above the surface of the basins. Water seeps laterally through the permeable strata of the beds and levees into the basins and maintains a high groundwater-table, which is generally not deeper than 2 ft. This groundwater is also fed by the numerous aquifers in the gravelly deposits underlying the cones. The river-banks and levees are free of groundwater, although in the latter a perched water-table is sometimes encountered.

The influence of the groundwater is most marked in the basins and the lagoon where the soils show a well-developed gley horizon above which a redox layer is formed, indicating fluctuations in the groundwater levels.

Apart from a weak mottling which occurs in places where a perched water-table is formed, the river-banks, levees, and cones do not show signs of gleying or similar effects of waterlogging.

(iii) *Calcium carbonate*

Another characteristic which is closely related to the relief is the occurrence of secondary lime precipitations in the soils.

Owing to the fact that a high percentage of the parent material is formed by calcareous rocks the soils are extremely high in $CaCO_3$. Values over 40 per cent. are not rare, but the mean percentage is about 15, which shows that, when the humid climate under which they occur is taken into account, the soils are still well preserved. Although often no visible signs of $CaCO_3$ are present in the soils they all react strongly to HCl.

According to the place of occurrence the $CaCO_3$ concentrates either as hard rounded concretions, in 'puppets', or in powdery form. The soils on the river-banks are freely drained and never contain concretions, while the $CaCO_3$ content of all the layers is about the same. In the levees lime occurs in a form similar to the river-bank soil. In these areas where water tends to percolate slowly, pseudo-mycelium or white flecks are more common. Rounded concretions occur generally where a perched water-table can be expected. In the basins the lime content in the subsoil is always higher than in the topsoil. Owing to the hydromorphic conditions and irrigation practice the $CaCO_3$ accumulates at lower depths in the profiles and it is often found in the so-called 'puppet' form. It is not quite clear whether these differences in concretionary forms are related to texture and compactness of soil or to variability of soil-moisture conditions.

Butler (1958, p. 13) has described similar characteristics of riverine plains in Australia where it appears that the lime content in the basins is lower than in the levees or river-banks.

In Mazanderan, however, the total $CaCO_3$ content in the whole

profile has proved to be the same and it accumulates only under specific conditions in certain layers. This dissimilarity might be explained by differences in weathering stages.

All the soils are weakly alkaline to alkaline with pH values ranging from 7·5 to 9·0 (pH in 1:2·5 soil/water suspension). In general, the pH's of the topsoils in the basins and the lagoon follow the $CaCO_3$ contents and they are commonly slightly less than those in the subsoil.

The soils have been grouped according to their places of occurrence, namely the different landscapes, and each group has been termed a *Soil Association*. This method has already proved its value for mapping purposes (C. H. Edelman, 1947, and J. J. van der Eyk, 1957), but in Mazanderan it served a much wider purpose because all the existing systems of land-use, irrigation layout, and density of population are equally well mapped in the same manner, namely by classifying the land according to the natural landscape units and their related soil associations.

The more elevated areas such as the river-banks and levees are used mainly for dry-foot crops of wheat, barley, cotton, and melons, while the low-lying basins and parts of the lagoon areas are devoted to paddy-rice. The irrigation layout on the levees differs considerably from that in use in the flat basins.

The population on the levee is concentrated in large, more or less square, villages, while in the basins the villages are long and narrow and are situated along the irrigation channels.

The soil associations may be grouped together in larger units in the more commonly used World Soil Groups (Table 2).

TABLE 2

Soil Classification in Mazanderan

Main soil group	*Soil association*
Mainly undifferentiated alluvial material	River-bank soils Levee soils Cone soils
Lithosols	Streambed soils
Regosols	Old dune soils (off-shore bar) Recent dune soils
Hydromorphic soils	Bottom lands or Basin soils Lagoon soils
Hydro-halogenic soils (Solonchak and ? Solonetz)	Slightly salty soils Severely salty soils

Note: Some associations of minor importance have been omitted.

Salty Soils

Apart from these soil associations which are related to the landscape, certain associations refer to salty conditions in the soil. The hydro-halogenic soils comprise the non-leached parts of the lagoon areas.

Most of the salty soils belong to the Solonchak group. Structure was

difficult to study in the area surveyed because the soils are normally very moist or wet. No definite Solonetz structure was seen.

The soils could be classified according to the system proposed by the U.S. Salinity Laboratory Staff (1954, pp. 4–5), which is based on the chemical characteristics of the soils. In practice, however, it was found that a broad division into slightly and severely salty soils was more suitable because of the very complicated pattern in which saline, saline/alkali, and non-saline alkali soils occur. This made accurate delineation on a semi-detailed level impossible.

A salt content indicated by 6 mmhos/cm. E.C. at 25° C. in saturation extract was used in distinguishing these two mapping units. Slightly salty soils are therefore defined by a salt content indicated by 4–6 mmhos/cm. E.C., while all the soils with an E.C. of more than 6 mmhos/cm. are classified as severely salty soils. In soils with an E.C. lower than 4 mmhos/cm. the percentage of exchangeable Na should not exceed 15, but where these conditions were found the soils were classed as severely salty.

In most cases, however, the salinity is caused by soluble sodium salts which tend to rise to the surface in the hot summer season owing to the high rate of evaporation. During winter most of the salty areas are submerged. This is caused by the considerable quantities of surplus water which are discharged into the lagoon by the numerous channels. The salts are then leached out to a certain depth in the profile, often the level of the groundwater, where they accumulate and rise again to the surface in the next summer season. This is illustrated by a white crust forming on the surface and the crystallization of soluble salts in veins in the capillary zone.

It is obvious that in these areas of the old lagoon, improvements in internal and external drainage together with prolonged leaching are necessary in any attempt to reclaim them. The drainage of these very impermeable soils, however, is very difficult. Drainage ditches about 4 ft. in depth would have to be excavated at relatively close intervals and the leachate pumped out of the area. This system which is similar to that applied in the Dutch Polders where salinization, caused by penetrating sea-water, is often a problem, might be used successfully in these salty areas.

Certain cultivators in Mazanderan have endeavoured to reclaim parts of the severely salty areas by flooding the land artificially for a year, after which they claim to obtain a reasonable rice crop. The depth of water necessary for this leaching has been calculated to be approximately 4 ft. per surface unit. The result of such practice has been investigated and soil samples were taken from an area before and after leaching process.

Table 3 indicates that the soluble sodium was leached out but the percentage of sodium in the adsorption complex increased. This shows that the original saline/alkali soil has become non-saline/alkali and a deterioration from the original condition had occurred. These analyses also indicate that a soluble calcium amendment such as gypsum or an acidulating material such as sulphur should be applied to replace the sodium in the adsorption complex.

Good yields were obtained in the area represented by profile 2, while the soil of profile 1 appeared to be unsuitable for rice-growing. This result indicates that the rice is more sensitive to sodium in the soluble form than in the adsorbed state. These yields might seem to be in contradiction to our applied classification of salty soils, according to which profile 2 is still regarded as severely salty. As explained above, the soils for which profile 2 is representative are improperly leached, as indicated by the chemical analyses, and we therefore consider them as unsuitable

TABLE 3

Reclamation of a Saline/Alkali Soil

Depth in inches	*E.C. in mmhos/cm. at 25° C. satn. extract*	*Exch.* Na *m.e.*	*Total exch. cap. m.e.*	*Sol.* Na *m.e.*
Profile 1—before leaching				
0–4	29·5	5·00	11·00	33·00
14–18	35·5	19·50	21·00	31·00
Profile 2—after leaching				
0–4	5·00	8·00	13·50	6·00
12–16	3·00	12·00	23·00	6·00

for paddy-rice irrigation, as after prolonged irrigation the increased salt content, which will occur as a result of bad natural drainage, prevents crop growth.

Some comparative analyses for the main soil associations are recorded in Table 4.

The yields of rice obtained on the various soil associations are in agreement with those quoted by H. Greene (1953) in respect of Punjab soils where a salt content of 0·24 per cent. and a pH lower than 6·8 give rise to similar yields.

Suitability for Irrigation of Paddy-rice

Much of the water which is used for irrigating paddy-rice in Mazanderan is applied to land which is nearest to the canals regardless of soil permeability. For this reason extensive areas of less permeable soils which are better suited to rice-growing cannot be irrigated from the existing water-supply and distribution systems. It was therefore of primary importance to classify the soils according to their irrigation need and secondly on their general suitability for paddy-rice growing. This implies that because of their high irrigation need in some instances, soils have been considered unsuitable for paddy-rice irrigation, although they are definitely capable of producing a good rice crop.

None of the available classification systems could be used for such a purpose as they are based on irrigation practices in respect of dry-foot crops as opposed to the flooded basins required for paddy-rice. A classification system was therefore developed specifically to group the soils according to their suitability for paddy-rice cultivation. The basic

TABLE 4 *Granulometric composition*

TABLE 4

Soil association	Depth in inches	% moisture	pH-H_2O	% $CaCO_3$	% C	Granulometric composition: 2 mm.–200 micron	200–50 micron	50–20 micron	20–2 micron	< 2 micron	% N	P_2O_5 Truog p.p.m.	Available K m.e./100 gr.	Total exch. cap. m.e./100 gr.	Exch. Na m.e./100 gr.	Soluble Na m.e./100 gr.	E.C. satn. extract E.C. × 10^3 at 25° C.
Leached severely salty lagoon soil	0–4	9	8·1	33	2·5	1	1	1	52	45	0·25	30	1·08	15·3	< 0·01	18·5	3
	8–12	13	7·9	19	1·1	1	1	30	23	45	0·19	0	1·28	20·0	< 0·01	86·9	16
	16–20	11	7·9	23	0·4	1	1	8	22	68	..	..	..	17·2	< 0·01	76·1	11
	28–32	7	8·0	19	0·6	1	1	1	20	77	..	..	..	22·6	< 0·01	93·5	20
	Capable of producing a rice crop of up to about 3,000 lb./acre (paddy).																
Salty basin soil	0–4	10	8·7	25	1·3	1	1	37	23	38	0·01	20	0·89	17·1	15·7	5·7	4
	6–12	9	8·3	30	0·5	1	1	1	76	21	0·08	0	0·35	12·0	10·1	18·3	26
	16–20	6	8·3	19	2·0	1	1	1	30	67	..	..	..	18·3	17·5	17·6	23
	32–36	6	8·4	13	0·2	1	1	64	64	19	..	..	..	13·2	10·1	12·3	16
	Rice failed to give satisfactory crop.																
Productive basin soil	0–4	11	7·9	17	1·3	1	4	1	30	64	0·26	80	1·40	22·3	0·01	1·1	1
	14–16	4	8·5	30	0·5	1	9	4	57	29	0·10	0	0·62	14·5	0·8	0·1	0
	24–30	5	8·6	32	0·2	1	1	1	50	47	..	..	..	15·1	0·8	0·1	0
	44–52	7	8·8	25	0·2	1	1	1	57	40	..	..	..	15·2	1·4	0·7	3
	Capable of producing a rice crop of up to 4,000 lb./acre (paddy) without fertilizing.																
Productive levee soil	0–4	1	8·3	14	1·1	1	3	23	53	20	0·12	10	1·42	11·3	..	..	..
	10–16	7	8·4	13	0·9	1	13	26	44	16	0·14	10	0·33	7·2	..	..	..
	18–24	1	8·5	16	0·6	1	39	37	16	7	..	..	..	1·8	..	..	..
	30–36	8	8·5	9	0·6	1	1	25	59	12	..	..	..	7·6	..	..	..
	44–52	4	8·7	9	0·6	1	2	15	67	15	..	..	..	7·9	..	..	..
	Capable of producing a rice crop of up to 4,000 lb./acre (paddy) without fertilizing.																

Note: The depths given are those at which the samples were taken. pH-H_2O in 1:2·5 soil/water suspension. Percentage C according to the Walkley-Black method. Percentage N according to the micro-Kjeldahl method.

Analysed by: Soils Laboratory, Royal Institute for the Tropics, Holland.

requirement is about 12 in. of saturated soil overlaying an impermeable soil layer of similar thickness in order to retain water on the surface of the soil.

In order to co-ordinate this system as far as possible with the method of land classification in use in Iran (F.A.O. Report No. 314, 1954) the terminology and codification as defined in that report were used wherever possible.

The criteria used in the classification which was developed during the survey were as follows:

1. Permeability
2. Depth of limiting layer.
3. Texture of topsoil.
4. Depth of water-table.
5. Salinity.
6. Flooding.
7. Slope.

1. *Permeability*

The *permeability* was assessed by examining the texture and structure.

2. *Depth to limiting layer*

A limiting layer was taken to be any layer which (i) is too permeable for making economic irrigation possible because of too high water consumption, and (ii) would impede root development.

In Mazanderan the limiting layer is mostly a sand or gravel layer which, according to the permeability classes used, are classified as rapidly permeable. On the other hand a layer of calcrete, although practically impermeable for water, is considered to be a limiting factor as well, as it hinders root development.

It must be understood that the limiting factor (i) (above) is purely based on irrigation need, while layers referred to under (ii) are considered to be an agriculturally limiting factor for satisfactory crop growth.

In both cases the layer must occur within the required soil depth of 2 ft., as below this depth no ill effect is caused to either irrigation need or root development, in which cases they are not regarded as limiting layers.

3. *Texture of topsoil*

Although rice grows well on soils of all textures, it has been found in Mazanderan that heavy soils are preferable to those of light texture. Optimum conditions are only met in the heavy clay soils. Grist (1955, p. 8) states that this opinion is generally accepted in tropical Asia. Topsoil refers to the part of the profile at a depth of 0–12 in.

4. *Depth of water-table*

In this classification the possibility of saline groundwater acting as a source of harmful salts which could rise to the surface was not taken into account. In terms of utilizing the available water resources as economically as possible, the height of the water-table was considered to be important and areas of permeable soils with high levels of groundwater were classified in a higher category than similar soils with a low water-table.

The following factors are not directly related to the consumption of irrigation water but in general they decrease the value of the soils considerably. Salinity is the main factor to be considered in Mazanderan, but the qualifications 'flooding' and 'slope' have been added as these factors might be of major importance elsewhere.

5. *Salinity*

The electrical conductivity values in millimhos per centimetre on saturation extracts were used to differentiate between soils which are slightly or severely affected by salts. The following classes were assumed:

0–4 mmhos/cm. salt free.
4–6 mmhos/cm. slightly salty.
More than 6 mmhos/cm. severely salty.

Soils with an E.C. less than 4 mmhos/cm. but with an exchangeable Na percentage higher than 15 were classified as severely salty soils.

6. *Flooding*

Flooding is likely to occur along streambeds, and for the purpose of this paper the term flooding is confined to inundation which cannot be controlled artificially. This factor has been classified according to the frequency of occurrence. In Mazanderan flooding occurs only after heavy rainfall in the low-lying basins and lagoon areas. This flooding is caused by inadequate surface drainage which could be improved and is therefore not a permanent land feature.

7. *Slope*

The slopes in alluvial plains rarely exceed 4 per cent. which is not considered excessive in the densely populated alluvial regions in Asia. Labour is generally plentiful in such areas and the work required for terracing steep slopes is not regarded as a serious limitation.

Distinction was made between the effective slope and the overall slope; the former being the slope of the terraces which are not always flat, while the latter refers to the slope of the land before terracing.

The overall slope limit of already terraced lands is 25 per cent. An overall slope of 14 per cent. of unterraced lands is regarded as the maximum slope which can be terraced economically under Asiatic conditions.

These criteria are subdivided and classified as follows:

Soil Features

Permeability of the Soil down to a Limiting Layer

Symbol	*Permeability class*	*Usual texture*
1	Rapid	Gravel to loamy sand
2	Moderate	Sandy loam to silty loam
3	Slow	Silty loam to silty clay loam
4	Very slow	Silty clay to clay

Depth of Limiting Layer

Symbol	*Depth*	*Description*
I	0–10 in.	Very shallow
II	10–24 in.	Shallow
III	24–40 in.	Moderately deep
IV	> 40 in.	Deep

Texture of Topsoil

Symbol	*Description*	*Texture*
Z	Very coarse	Gravel to sand (coarse)
C	Coarse	Fine sand
L	Light	Sandy loam
M	Medium	Loam to silt loam
H	Heavy	Silty clay loam
V	Very heavy	Silty clay to clay

Depth of Water-table

Symbol	*Depth*	*Description*
a	0–10 in.	Very high
b	10–40 in.	High
c	40–60 in.	Moderate
d	> 60 in.	Deep

Salinity

Symbol	*Description*	*Norms*
S1	Slight	4–6 mmhos/cm. at 25° C.
S2	Severe	< 4 mmhos/cm. at 25° C. and exch. Na > 15% > 6 mmhos/cm. at 25° C.

Landscape Features

Flooding

Symbol	*Description*	*Norms*
F1	Slight problem	Probably once in 6–10 years
F2	Moderate problem	Probably once in 3–5 years
F3	Severe problem	Probably once in 1–2 years

Slope

Symbol	*% slope*	*Description*
A	Flat	Non-terraced land
	Flat	Terraced slopes with overall slope not exceeding 2%
B	0–2	Non-terraced slopes
	0–2	Terraced slopes with overall slopes not exceeding 4%
C	2–4	Non-terraced slopes
	2–4	Terraced slopes with overall slopes not exceeding 8%
D	4–8	Non-terraced slopes
	4–8	Terraced slopes with overall slopes not exceeding 14%
E	8–14	Non-terraced slopes
	8–14	Terraced slopes with overall slopes not exceeding 25%
F	Non-terraced slopes exceeding 14%	
	Terraced slopes exceeding 25% overall slope	

By using these symbols in the order shown it was possible to describe every soil site examined by means of a formula illustrated by the following examples:

(i) $\frac{3/II/H/b}{A}$. This is a soil with a slow permeability to a depth of 24 in. and a silty clay loam topsoil. The water-table is within the range of 10–40 in.

(ii) $\frac{4/III/V/b/S2}{F1/A}$. This is a soil with a slow permeability to a maximum depth of 40 in. The topsoil is a silty clay to clay. The water-table is found within the range of 10–40 in. The limitations are severe salinity and flooding once in 6–10 years.

It will be noticed that the soil characteristics form the numerator while the land factors form the denominator of the fraction.

This system enables one to classify the soils in terms of their suitability for paddy-rice irrigation.

Six classes which conform to the standards outlined in schematic form in Table 5 have been distinguished.

Classes IV and V are applicable to soils which are temporarily unsuitable for irrigation owing to limitations which can be improved. After amelioration these classes can be raised to Class I, II, or III, depending on the circumstances.

In Mazanderan the limitations imposed by salinity were the only reasons for placing soils in Classes IV and V.

Soils which are classified as Class VI cannot be improved owing to

TABLE 5

Standards for Classification of Soils according to their Suitability for the Irrigation of Paddy-rice

	Criteria						
	Soil Features				*Land Features*		
Irrigability classes	*Permeability*	*Depth to limiting layer*	*Texture of top-soil*	*Salinity*	*Water-table*	*Risk of flooding*	*Slope*
Class I. Excellent	Slow to very slow	Deeper than 40 inches	Silty clay or heavier	None	No limitation	None	Flat terraces with overall slopes not exceeding 2%. Level lands
Class II. Good	Slow to very slow	Deeper than 24 inches	Loam or heavier	None	No limitation	None	0–2% terraced slopes with overall slopes $<8\%$. 0–2% non-terraced slopes
Class III. Fair	Moderate to very slow	Deeper than 24 inches	Sandy loam or heavier	None	In case texture is light water-table must be shallower than 40 in.	Probably once in 6–10 years	0–4% terraced slopes with overall slopes $<14\%$. 0–4% non-terraced slopes
Class IV. Suitable with qualifications	Moderate to very slow	Deeper than 24 inches	Sandy loam or heavier	Slight 4–6 mmhos/cm. at 25° C. E.C. in satn. extract	No limitation	Probably once in 3–5 years	0–8% terraced slopes with overall slopes $<25\%$. 0–8% non-terraced slopes
Class V. Only suitable after radical amelioration	Moderate to very slow	Deeper than 24 inches	Sandy loam or heavier	Severe >6 mmhos/cm. E.C. at 25° C. in satn. extract <4 mmhos/cm. and exch. Na $>15\%$	No limitation	Probably once in 3–5 years	0–14% terraced slopes with overall slopes $<25\%$. 0–14% non-terraced slopes
Class VI. Unsuitable	Any soil which does not qualify for Classes I–V						

particular land or soil features and are regarded as permanently unsuitable.

In practice this system has proved its value in Mazanderan where the irrigability classes often coincide with the recognized soil associations and actual crop yields.

In Figs. 4 and 5 examples are given which show how the soil-association map has been adapted to show the suitability of these soils for irrigation.

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REFERENCES

BUTLER, B. E. 1958. Depositional system of the riverine plain of South-Eastern Australia in relation to soils. C.S.I.R.O. Soil Publ. No. 10, 11–16.

DEPARTMENT OF AGRICULTURE, RIVERSIDE, CALIFORNIA. 1954. Diagnosis and improvement of saline and alkali soils. Agricultural Handbook No. 60.

EDELMAN, C. H. 1947. Over de Bodemgestelheid van Midden-Nederland.

EYK, J. J. VAN DER. 1957. Reconnaissance soil survey in Northern Surinam. Thesis accepted for the degree of Doctor of Agriculture, Wageningen.

GREENE, H. 1953. Using salty land. F.A.O. Agricultural Study No. 3, 15–18.

GRIST, D. H. 1955. Rice. Longmans, Green, London.

JOFFE, J. S. 1949. Pedology. Somerset Press, New Jersey.

KEUNEN, H. 1950. Marine Geology. John Wiley, New York.

UNITED NATIONS FOOD AND AGRICULTURE ORGANIZATION. 1954. Soil conservation and land classification in Iran. F.A.O. Rep. No. 314.

UNITED STATES DEPARTMENT OF AGRICULTURE. 1951. Soil Survey Manual. Agricultural Handbook No. 18.

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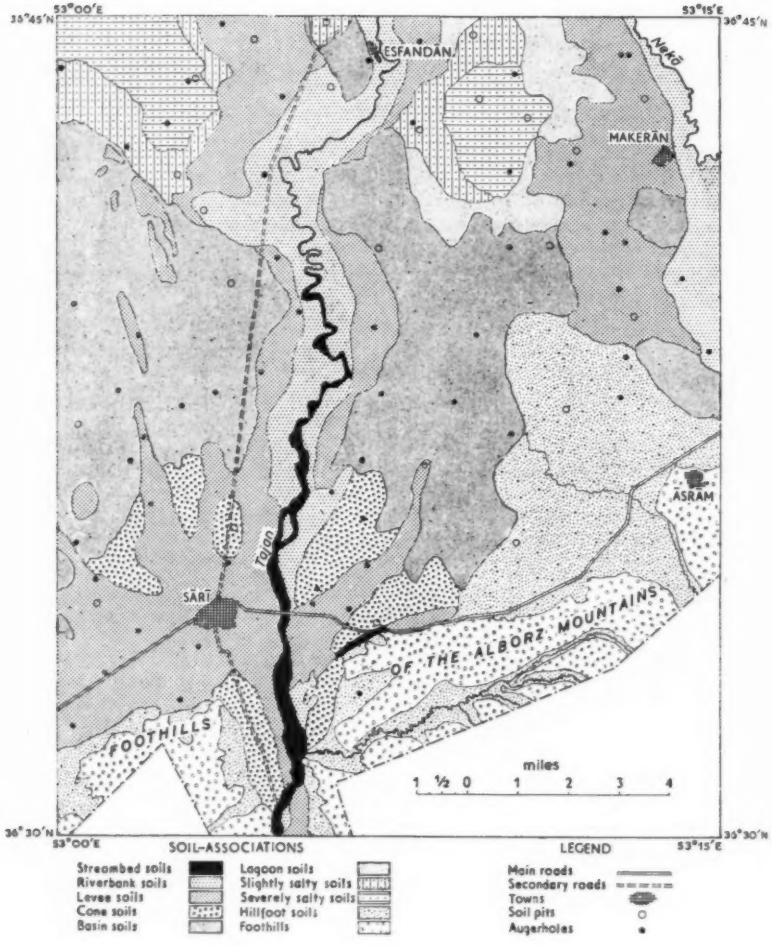

FIG. 4. Soils map.

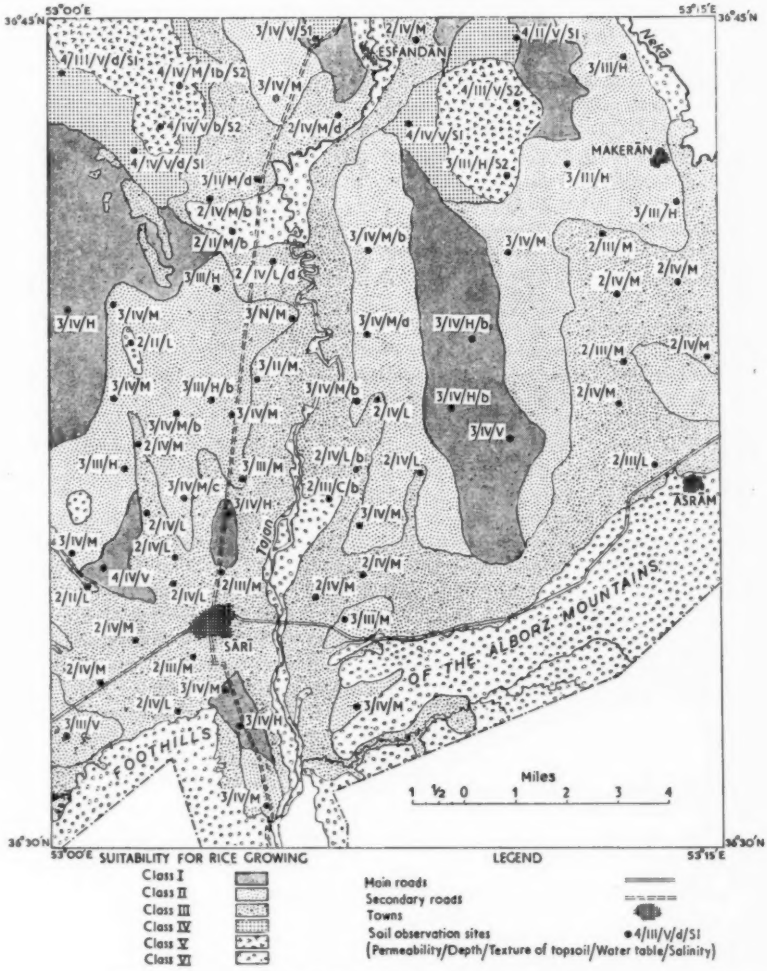

FIG. 5. Land classification for the purpose of rice-growing.

STUDIES ON A NIGERIAN FOREST SOIL

I. THE DISTRIBUTION OF ORGANIC MATTER IN THE PROFILE AND IN VARIOUS SOIL FRACTIONS

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Summary

Features of the profile of a mid-slope forest soil typical of the red concretionary variant of the Iwo Series, which is common in Western Nigeria, are the well-defined gravel horizon from 7 to 50 in., and the sandy horizon above it.

The carbon content in the top 2 in. is 3·95 per cent. There is a very sharp fall to 0·38 per cent. below 2 in. The percentage carbon then decreases slowly down the profile. The C/N ratio is also high in the worm casts (15·7) and topsoil (13·6); below 2 in. it is much lower, and falls to 3·1 at 60 in. Both the root growth and worm activity are confined to the top few inches of the profile.

The pH in the 0–2 in. horizon is 7·7, representing a considerable accumulation of bases in the surface soil. Below 2 in. the pH is fairly constant at about 6·7 down to 50 in., when it falls again to 5·6.

Although contributing only 2·5 per cent. to the weight of the top 4 in. of soil, the plant residues comprise 17·3 per cent. of the organic matter in this layer. Most of the organic matter, however, is in the coarse-silt aggregate fraction. After removal of plant residues, the C/N ratio of the remaining fine-earth fractions falls as the particle size of the fraction decreases.

Aggregation in the surface soil is caused by organic matter, but at 20–30 in. aggregation is due to the high free iron oxide. Extraction of the aggregate fractions with 0·5 M sodium hydroxide and 0·1 M sodium pyrophosphate (pH 7) indicates the varying nature of the organic matter in these fractions.

Introduction

In a tropical forest, in spite of a high litter fall, the proportion of carbon on the forest floor to the total carbon in the profile is usually low, being about 1 per cent. as compared with 11 per cent. for a temperate oak forest (Jenny, 1950). Leaf fall in such a rain forest is rapidly attacked by soil animals and saprophytic organisms, and there is generally only a very thin layer of dead and rotting vegetation lying on the soil surface. The author estimates that, under suitable conditions, an individual leaf loses its structure in 14–21 days after falling. The organisms decomposing this vegetation in the tropics do not seem to produce humus in the *temperate* sense of the word (Russell, 1950), and although the soil may contain high amounts of carbon and nitrogen, the organic matter has a much lighter colour. Vageler (1933) went so far as to state that it is possible that the humus in all well-drained tropical soils is lighter in colour than in soils from temperate regions.

From extrapolation of the nitrogen-temperature curves of Jenny (1930) to the high annual temperatures of the tropics, tropical soils were expected to be low in organic matter and nitrogen. Under natural vegetation in the humid tropics, however, it is common to find surface soils with fairly high organic-matter and plant-nutrient contents over poor

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acid subsoils. Several workers have attempted to elucidate the apparent differences in behaviour between temperate and tropical soils in following Jenny's theory. Examining some equatorial soils of Colombia, Jenny (1948) found that within constant moisture belts, the nitrogen and organic matter increased exponentially as the average annual temperature decreased through the range 30° C. to 10° C. Birch and Friend (1956) found that the main factor affecting the stability of soil organic matter in the tropics was rainfall. Temperature and clay content of the soil were minor factors, except in very sandy soils.

Although undecomposed plant material and humified substance play different roles in the general effects of organic matter on soil properties, few attempts have been made to separate these physically. Lein (1940) applied the method of centrifugal separation of minerals with heavy liquids to soils and examined the fractions he obtained with a microscope. He concluded that the lighter fractions contain 'free' organic matter consisting of partly decomposed plant residues, humates, and humic acid, and that the heavier fraction contained fulvic-like complexes combined with, or absorbed on, mineral substances. Hénin and Turc (1949) described a similar density method using mixtures of benzene and bromoform. They distinguished two main fractions, the lighter one consisting mainly of plant residues and having a high C/N ratio; in the other the organic matter was closely bound to mineral matter and had a low C/N ratio.

A method of measuring plant-residue fragments in soil was reported by McCalla *et al.* (1943), who separated three fractions readily identified as plant residues. These were (*a*) plant material greater than 3 mm., (*b*) plant material between 3 mm. and 0·4 mm., (*c*) material less than 0·4 mm. retaining its cellular structure.

This paper presents the data obtained by examining a mid-slope forest profile near Ibadan, Western Nigeria, with particular reference to the distribution of organic matter in the profile and in various soil fractions. A method of separating plant residues is given, with an aggregate analysis of the remaining mineral matter.

Description of Site and Soil Profile

The land form developed over the gneisses around Ibadan consists of an undulating plain with an average altitude of 700 ft., draining towards the sea 70 miles to the south. The average annual rainfall at Ibadan is 48·4 in. There are two rainy seasons with maximum falls in June and September, a short relatively dry period in August, and a 4-month dry season from November to February. Both dry seasons vary considerably in duration and intensity, and heavy irregular storms often occur in December and January. The relative humidity at mid-day is highest in July, 78 per cent., and lowest in February, 49 per cent.; the average annual temperature is 80° F. with little variation in the monthly average. The natural vegetation is broadly classified by Keay (1953) as 'lowland rain forest' (Plate I, Fig. 1). This vegetation, in the Forest Reserve where the soil samples were collected, is known to be undisturbed for at least 50 years, but the earlier history is unknown.

The forest floor is covered by a very thin layer of dead and rotting vegetation, which in places is not thick enough to cover the surface of the soil. There is, however, a thick carpet of worm casts intermingled with this plant debris (Plate I, Fig. 2). These casts are produced by the species *Hippopera nigeriae* (Taylor, 1949) at a prolific rate during the rainy season. In the dry season, worm activity is much reduced, except near streams and other low-lying wet areas. The casts are very characteristic in appearance (Plate II, Fig. 1), being quite different from those produced by the common British species of worms. The irregular cylinders, up to 7 cm. long and 2·9 cm. in diameter, stand vertically on the surface of the soil when fresh. There is a small hole running through the centre of the cast almost to the top, which is sealed. The worm lies just under the surface, and builds up the cast by extruding earth circularly around the tip of its tail, which it gradually pushes upwards through the extruded mass. As the casts age they fall, and lie horizontally on the ground until the rain breaks them down to a fine sandy loam which forms the Cr W horizon described by Nye (1954).

The profile studied is representative of the Iwo Series which has been grouped by Vine *et al.* (1954) as a sedentary member of the Ibadan Fasc. The series is derived from coarse granitic rocks and coarse gneisses, and is well drained. Traces of feldspar are often seen in the profile to a depth of 4 in. The main features of this series are the presence of a gravel-concretion horizon in the upper part of the profile (Plate II, Fig. 2), and the lack of development of a deep mottled clay layer, a feature which is very common in soils derived from the equally widespread medium and fine-grained metamorphic rocks. Weathered rock *in situ* is usually reached at about 5–6 ft.

The Iwo Series is common in that part of the Western Region of Nigeria underlain by metamorphic rocks of the Old Basement Complex.

The particular profile studied in this paper is typical of the Red Concretionary variant of the Iwo Series; it differs from the normal variant in being sandy in the top 10 in. and in containing frequent concretions at about 25 in. depth.

Site: Mid-slope.

0–2″ Dark reddish-brown (5 YR 3/2), humic loamy fine sand with fragments of worm casts and many fine roots; weak fine crumb structure; changing sharply to

2–7″ Reddish-brown (5 YR 3/4), loose sand with many roots; very few angular quartz gravel; very few small hard pisolitic concretions; merging to

7–12″ Reddish-brown (5 YR 4/4), loamy coarse sand; few angular quartz gravel and stones; frequent hard small pisolitic concretions; few roots; changing clearly to

12–20″ Brown (2·5 YR 3/4), coarse sandy loam to coarse sandy clay loam; few angular quartz gravel and stones; frequent to very frequent concretions (mainly pisolitic iron concretions with some soft concretions containing manganese oxides); structureless; (Plate III, Fig. 1) traces of roots; merging to

20–30″ Reddish-brown (2·5 YR 3/6), sandy clay loam; very few angular quartz gravel and stones; frequent concretions—both iron and manganese; structureless; changing irregularly but clearly to

30–40″ Red (2·5 YR 4/6), brownish-yellow (7·5 YR 5/6) and black mottled, breakable hardpan with few small pisolitic concretions.

44–60″ Brown, reddish-brown, brownish-yellow, and red mottled hardpan and feldspathic rock material with iron and manganese staining; frequent angular vein quartz fragments; merging to

60–72″ Weathered acidic rock stained with iron and manganese.

Experimental

Soil sampling

A large sample of surface soil, 0–4 in., was taken after removing the surface litter from about 4 sq. ft. Inside this, 1 sq. ft. was marked out and the soil, roots, &c., carefully removed to a depth of 4 in. This was repeated for 20 sites in the forest and the bulked samples air-dried in the laboratory. Large roots were removed by hand and discarded, and the sample gently pulverized and passed through 1 mm. sieve. At one of the sampling sites the above profile pit was dug to a depth of 6 ft., and samples of the profile were taken in the normal manner, air-dried and sieved. Samples of undecomposed and decomposing forest litter and worm casts were also collected. All sampling was carried out during the months of May and June, i.e. during the early rains.

Carbon. Total carbon was determined by the Walkley and Black method (1934), corrected for 77 per cent. recovery.

Nitrogen. Nitrogen was determined by a semi-micro Kjeldahl procedure using commercial selenium dioxide, copper sulphate, and sodium sulphate tablets as catalysts. Markham's (1942) distillation apparatus was used, the ammonia being collected in 2 per cent. w/v boric acid containing 25 ml. per litre of Conway and O'Malley's (1942) indicator. About 30 ml. of distillate were collected and titrated with N/140 sulphuric acid. Frequent blank determinations on reagents and controls with a standard (N/140) solution of ammonium sulphate were carried out.

Extraction of soil fractions with 0·5 M sodium hydroxide and 0·1 M sodium pyrophosphate (pH 7·0). Before extraction all samples were leached with cold 0·1 N HCl to remove carbonates, exchangeable bases, and inorganic nitrogen, and then washed thoroughly with distilled water. The acid-leached and washed samples were then used directly in the extractions. Ten grammes of oven-dry sample (as originally weighed before acid-leaching) was treated with 100 ml. of 0·1 M sodium-pyrophosphate (pH 7·0) or 0·5 M sodium-hydroxide extractant. The suspensions were mechanically shaken for one hour, left standing for 22 hours with occasional hand shaking, and finally shaken mechanically for another hour.

The suspension was allowed to settle for one hour and the supernatant liquid siphoned off and centrifuged. The residue was washed by shaking with distilled water, allowing to settle, and siphoning and centrifuging as before. The washing was repeated once more, and the residual slurry was coagulated by the addition of a few drops of dilute hydrochloric acid. The residue was filtered off, washed on the filter with distilled water

until the filtrate was pH 7, then oven-dried and weighed. It was ground to pass a 70 I.M.M. (180 μ) sieve before analysis.

Free iron oxide was extracted with hydrosulphite, according to the method of Mackenzie (1954).

Exchange properties. Exchange acidity was determined by Schofield's (1933) method, and pH with the glass electrode, using a 2·5 : 1 water/soil ratio.

Separation of plant-residue fragments and fractionation of water-stable aggregates. The raw material for the separation was the top 0–4 in. of air-dried soil, passing a 1-mm. sieve.

The soil was wet-sieved through a 70 I.M.M. sieve (aperture 180 μ). About 50 g. soil was placed in the sieve and lightly brushed in distilled water until no more solid was washed through. The material left on the sieve was a mixture of coarse sand and plant residues. This was separated by flotation and decantation. The residues were filtered off, washed with distilled water, and oven-dried at 105° C. The coarse sand was also oven-dried at 105° C.

The effluent from the sieving contained soil material less than 180 μ, ranging from fine sand to clay. The solids were fractionated by varying maximum sedimentation rates. This was carried out in the distilled water used for the preliminary sieving, and no attempt was made to disperse aggregations.

The sedimentation was carried out over 25 cm. in 30-cm. sedimentation cylinders. At a convenient time the suspension was stirred, until the sediment was removed from the bottom of the cylinder. The stirrer was removed and the time of commencement of sedimentation was noted. For the first fraction the rate of sedimentation was 10 cm. in 48 seconds (or 2 minutes for the 25 cm.). About 10 seconds before the time of sedimentation elapsed, siphoning of the supernatant liquid was commenced. During the siphoning period the level of liquid in the cylinder was followed by the top end of the siphon. The siphoning usually took about 20 seconds, so that all settling times were reported as $\pm$10 seconds. The first sediment was fine sand, and it was necessary to wash and decant off some dark particles which were returned to the suspension. Microscopic examination of the fine sand fractions, after several decantations and final drying at 105° C., showed clean sand particles containing only a trace of organic matter.

Two other sediments were collected: coarse silt consisting of particles and aggregates having a maximum sedimentation rate of 10 cm. in 5·2 minutes (25 cm. in 13 minutes)—the settling and siphoning being carried out as above; and silt with a sedimentation rate of 10 cm. in 8 hours (25 cm. in 20 hours). For both sediments the thick slurry left in the cylinder after siphoning off the supernatant liquid was filtered, washed with distilled water, and dried in an oven at 105° C.

The clay suspension was acidified with a small excess of hydrochloric acid, and set aside to flocculate. The clear supernatant liquid was siphoned off as completely as possible and the residue washed into a beaker. After further siphoning the clay residue was evaporated to dryness and dried in an oven at 105° C.

Discussion of Experimental Results

1. *The profile*

A selection of the analytical data of the profile is given in Table 1. The features of the profile are typical of a soil developed in the tropics from a parent rock which consists mainly of coarse granites and coarse-grained gneisses. The top 7 in. are sandy, and there is a marked stone/gravel layer between 7 and 50 in. with a maximum gravel content of over 80 per cent. between 12 and 20 in. The horizons discussed by Nye (1954)

TABLE 1

Some Analytical Data of the Profile

	Worm casts	0–2″	2–7″	7–12″	12–20″	20–30″	30–40″	40–50″	60–72″
Total stones over 1 mm. (%)	nil	10	33	63	81	71	56	53	29
Concretions over 1 mm. (%)	nil	1·4	16	40	54	59	49	41	9
Quartz gravel over 1 mm. (%)	nil	8·6	17	23	27	12	7	12	20
Mechanical analysis									
1·0–0·2 mm. (%)	17	29	33	18	8·5	9·6	11	..	..
0·2–0·02 mm. (%)	38	39	26	11	6	7·8	8·8	..	..
0·02–0·002 mm. (%)	32	12	5·4	4·4	2·1	4·9	10	..	..
< 0·002 mm. (%)	13	10	2·6	3·6	2·4	6·7	14·2	..	..
pH	7·1	7·7	6·4	6·7	6·7	6·7	..	6·5	5·6
Exchangeable H (m.e./100 g.)	..	0·6	1·1	1·1	1·3	2·3	..	2·0	2·0
Free Fe_2O_3 in fine earth (%)	1·22	1·15	1·05	1·47	3·6	4·8	6·4	6·4	..
Carbon (%)	6·9	3·95	0·38	0·30	0·22	0·21	..	0·21	0·05
Nitrogen (%)	0·44	0·29	0·047	0·043	0·032	0·026	..	0·030	0·016
C/N ratio	15·7	13·6	8·1	7·0	6·9	8·1	..	7·0	3·1

can easily be identified, although they vary in detail from those he described. Mechanical analysis shows that the worm casts contain relatively little coarse sand and 88 per cent. of this is between 0·2 mm. and 0·5 mm., but the fine-sand content is fairly constant in the casts and the top 7 in. of the profile. The silt fraction is high in worm casts, and it will be seen from the data that the worms transport silt and clay to the surface from lower parts of the profile. It is unlikely, however, that the worms operate much below 12 in. The termite-formed horizon, 2 in. to 7 in., is almost gravel-free in the upper part, but its lower boundary merges with the gravel layer between 7 in. and 12 in. Quartz gravel is concentrated in the 12–20 in. layer, but the maximum concentration of concretions appears a little farther down the profile.

The pH is high in the worm casts and topsoil, 0–2 in., but remains fairly constant thereafter, 6·4–6·7, to a depth of 5 ft.; it then falls to 5·6. The surface accumulation of bases is generally attributed to the action of vegetation in transferring cations from the root zone to the surface litter. The decomposition of this litter appears to be limited mainly to the top 2 in. The amounts of free iron oxide in the profile fine-earth samples increase to a depth of 5 ft., probably due to the increasing proportion of relatively iron-rich clay in the soil.

Fractionation of profile samples. Fine-earth samples from the profile

were fractionated by the method described. The plant residues smaller than 1 mm. are high in the worm casts and 0–2 in. horizon, but below 2 in. there is a very sharp fall, and only traces of roots are found below 12 in. (Plate III, Fig. 1). In the fractionation of the remainder of the sample there was no dispersion, and the fractions contain water-stable aggregates of the various sizes (Table 2).

TABLE 2

Aggregate Analysis of Fine Earth in the Profile (as Percentage of Total Fine Earth)

	Worm casts	0–2″	2–7″	7–12″	12–20″	20–30″
Plant residues	3·7	2·1	0·06	0·03	trace	trace
Coarse sand	17	30	51	42	34	38
Fine sand	38	34	32	16	28	23
Coarse-silt size	34	26	8	23	27	31
Silt size	4·1	5·0	5·4	7·3	7·9	7·4
Clay	1·04	0·71	2·6	9·6	1·8	0·3

The coarse-silt-size fraction contains discrete particles and aggregates in the size range 0·02–0·05 mm.; the silt-size fraction contains discrete particles and aggregates in the size range 0·002–0·02 mm. These size ranges are not strictly accurate, since an aggregate might be less dense than a discrete mineral particle of the same size, and therefore settle at a lower rate. Alderfer and Merckle (1941) proposed a similar aggregate analysis, and compared the results obtained with those from a normal mechanical analysis. This comparison formed the basis for the introduction of a figure designated as the 'stability index' to describe the stability of the soil structure. A similar single-value constant is the 'dispersion ratio' defined by Middleton (1930) as

$$\frac{(\text{clay}+\text{silt in undispersed soil})}{(\text{clay}+\text{silt in mechanical analysis})} \times 100.$$

The 'dispersion ratios' for the samples down the profile are shown in Fig. 1. Aggregation (the inverse of the dispersion ratio) is high in the top 2 in. but there is a marked fall, which continues to 12 in., in the 2–7 in. horizon. Below this the aggregation increases again until at 30 in. it is as high as in the surface soil. The reason for these changes in aggregation became apparent when examined together with changes in organic matter and free iron oxide in the profile.

In the top soil the organic matter is effective in aggregating the smaller particles. The worm casts have a dispersion ratio of 11·1, i.e. a high degree of aggregation (as might be expected from the high organic-matter content). The sharp drop in carbon content below 2 in. is reflected in an almost equally sharp fall in aggregation—the free iron oxide being fairly constant in the first 12 in. Minimum aggregation (maximum dispersion ratio) occurs at 7–12 in. when both carbon and free iron oxide are low. Below 12 in. a steady increase in free iron oxide results in a

corresponding increase in aggregation. The role of free iron in aggregation is not properly understood. Its aggregating influence in the lower parts of this profile can most likely be ascribed to cementation due to precipitation of hydrated iron gel and its irreversible dehydration. To the methods listed by Deb (1950) for the movement of iron down the profile can be added the process of illuviation of the relatively iron-rich

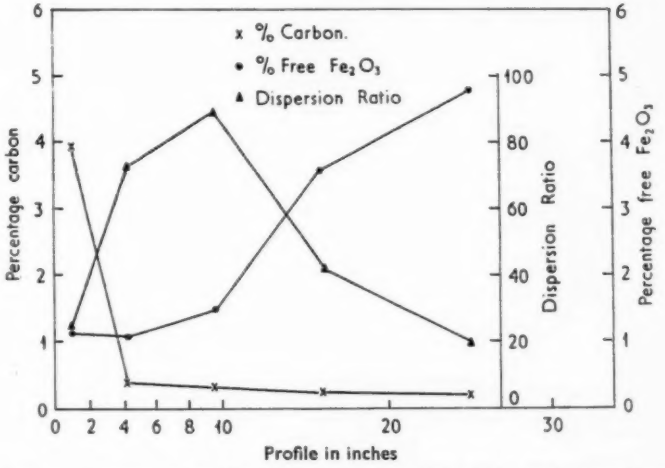
x % Carbon.
• % Free Fe_2O_3
▲ Dispersion Ratio
Percentage carbon
Dispersion Ratio
Percentage free Fe_2O_3
Profile in inches
0 2 4 6 8 10 20 30
0 1 2 3 4 5 6
0 20 40 60 80 100

FIG. 1. Percentage carbon, percentage free iron oxide, and dispersion ratio in the profile.

TABLE 3

Percentage Carbon Content of Aggregate Fractions in the Profile

	Worm casts	0–2″	2–7″	7–12″	12–20″	20–30″
Coarse silt . . .	17·8	12·1	1·6	0·6	0·6	0·4
Silt	12·0	10·4	1·7	0·9	0·5	0·5
Clay	12·4	9·7	1·3	1·0	0·7	0·9

clay in the well-drained soil described. This is in contrast to an explanation of the development of the iron-oxide concretions that requires mobilization followed by relatively irreversible deposition of the iron (Nye, 1955).

The carbon contents of some of the aggregate fractions in Table 2 are shown in Table 3.

It is interesting to note that whilst in the topsoil with a high C/N ratio of 13·6 the coarse silt has the highest carbon content, in the 20–30 in. horizon, which has a low C/N ratio of 8·1, the carbon content of the clay fraction is over twice that of the coarse-silt fraction. This agrees with the observations on aggregation, i.e. that the aggregation due to organic matter decreases with depth, and the aggregation at 20–30 in. is mainly

due to free iron oxide. The low C/N ratio in the lower parts of the profile is associated with the clay. Rodrigues (1954) explained this marked decrease in C/N ratio with depth in some tropical profiles by his finding that the proportion of soil nitrogen in the form of fixed ammonium ion increased with depth in these profiles. This type of fixation is usually explained by the penetration of the ammonium ions into the interior of the lattice structure of clay minerals that have the appropriate space dimensions, where they replace the interlayer cations. Present evidence indicates that the clay minerals chiefly responsible are illite, vermiculite, and montmorillonite.

2. *The organic matter in the 0–4 in. sample*

The 0–4 in. bulk sample (20 kg.) was fractionated as described earlier; the results of the fractionation, together with carbon, nitrogen, and C/N ratios of the fractions, are given in Table 4.

TABLE 4

Organic Matter in the Fractions from 0 to 4 in.

	Total fine earth	*Plant residues*	*Coarse sand*	*Fine sand*	*Coarse silt*	*Silt*	*Clay*
% in soil, O.D. basis	..	2·5	29·0	28·9	28·7	8·6	1·1
Carbon in fraction (%)	3·95	26·5	0·1	0·1	8·3	7·5	5·5
Carbon in fraction as % of total carbon in soil	..	17·3	0·8	0·8	63·3	16·6	1·5
Nitrogen in fraction (%)	0·29	1·73	..	..	0·71	0·70	0·64
C/N ratio of fraction	13·6	15·3	..	..	11·7	10·7	8·6

Although the plant residues contribute only 2·5 per cent. to the weight of the topsoil, they contain 17·3 per cent. of the organic matter. Apart from the easily identified small rootlets, this fraction contains a considerable amount of miscellaneous small debris (Plate III, Fig. 2). Some seed cases, fungal spores, pollen grains, and pieces of insect casings were positively identified. A careful microscopic examination of the smaller aggregation fractions, coarse silt, silt, and clay showed that, at least in the soil examined, there were no identifiable plant or animal fragments present. The smallest intact fragments of plant or animal observed in the residue fractions were about 0·1 mm. (100 μ); this probably represents the lower limit as determined by the fauna present in this soil.

The sand fractions contained so little organic matter that they were not considered further; although constituting 57·9 per cent. of the total fine earth, coarse and fine sands together contain only 1·6 per cent. of organic matter, and this is probably contamination by the smaller fractions. By far the biggest part, 63·3 per cent., of the organic matter is found in the coarse-silt-size fraction.

The C/N ratio of the organic matter in the fractions also varies considerably, being highest, 15·3, for plant residues and lowest, 8·6, for the clay.

By extracting each soil fraction with 0·5 M sodium hydroxide and

0·1 M sodium pyrophosphate (pH 7·0), the differences in the nature of organic complexes present in the fractions are emphasized (Table 5). There is no constant relation between the C/N ratio of each fraction and the extracts obtained from each fraction. In some cases the ratio is greater in the fraction than in the extracts, in others smaller. There is less difference between the ratios of fraction and extract for sodium

TABLE 5

Extraction of Fractions from 0 to 4 in. with 0·5 M Sodium Hydroxide and 0·1 M Sodium Pyrophosphate (pH 7·0)

	Carbon extracted as % of total C *in fraction*		*Nitrogen extracted as % of total* N *in fraction*		C/N *ratios*		
					Extracts		
	Sod. hyd.	*Sod. pyro.*	*Sod. hyd.*	*Sod. pyro.*	*Orig. fract.*	*Sod. hyd.*	*Sod. pyro.*
Plant residues . .	44·3	7·4	38·6	0·7	15·3	17·6	14·7
Coarse silt . .	50·4	24·3	49·7	16·3	11·7	11·8	17·4
Silt . . .	46·3	27·6	48·2	21·7	10·7	10·6	13·7
Clay . . .	60·2	69·0	61·8	67·3	8·6	8·2	8·8

TABLE 6

Effect of Acid-leaching on the Amount of Carbon Extracted by Sodium Hydroxide

	Carbon extracted as % of total C *in fraction*	
	Without acid-leaching	*With acid-leaching*
Plant residues . .	33·0	44·3
Coarse silt . . .	15·8	50·4

hydroxide than for sodium pyrophosphate. Alkali extracts more nitrogen in relation to carbon than does neutral pyrophosphate solution, from all fractions except the plant residues.

The effect of acid-leaching, previous to extraction with sodium hydroxide, on the amount of organic matter extracted is considerable, being much larger, however, for the coarse-silt fraction than for the plant-residue fraction (Table 6).

The amounts of carbon and nitrogen extracted by alkali do not vary much from fraction to fraction, about half of the organic matter in each fraction being extractable. Extraction with pyrophosphate, however, shows big differences between fractions. Only 7·4 per cent. of the carbon and 0·7 per cent. of the nitrogen in the plant residues is extractable, while for clay the pyrophosphate extracts even more than the alkali, 69·0 per cent. of the carbon and 67·3 per cent. of the nitrogen.

Acknowledgements

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REFERENCES

ALDERFER, R. B., and MERCKLE, F. G. 1941. Soil Sci. **51,** 201.
BIRCH, H. F., and FRIEND, M. T. 1956. J. Soil Sci. **7,** 156.
CONWAY, E. J., and O'MALLEY, E. 1942. Biochem. J. **36,** 655.
DEB, B. C. 1950. J. Soil Sci. **1,** 112.
HÉNIN, S., and TURC, L. 1949. C. R. Acad. Agric. **35,** 41.
JENNY, H. 1930. Missouri Agric. Exp. Sta. Res. Bull. 152.
—— 1948. Soil Sci. **66,** 173.
—— 1950. Ibid. **69,** 43.
KEAY, R. W. J. 1953. An Outline of Nigerian Vegetation. Government Printer, Nigeria.
LEIN, Z. Ya. 1940. Pedology, **10,** 41.
MCCALLA, T. M., *et al.* 1943. Soil Sci. **55,** 159.
MACKENZIE, R. C. 1954. J. Soil Sci. **5,** 167.
MARKHAM, R. 1942. Biochem. J. **36,** 790.
MIDDLETON, H. E. 1930. U.S.D.A. Tech. Bull. 78.
NYE, P. H. 1954. J. Soil Sci. **5,** 7.
—— 1955. Ibid. **6,** 51.
RODRIGUES, G. 1954. Ibid. **5,** 264.
RUSSELL, E. W., and RUSSELL, E. J. 1950. Soil Conditions and Plant Growth. 8th edition. Longmans, London.
SCHOFIELD, R. K. 1933. J. Agric. Sci. **23,** 252.
TAYLOR, A. G. 1949. Proc. Zool. Soc. Lond. **119,** 703.
VAGELER, P. E. 1933. An Introduction to Tropical Soils. Macmillan, London.
VINE, H., *et al.* 1954. Proc. 2nd Inter-Afr. Soils Conf. **1,** 211.
WALKLEY, A., and BLACK, I. A. 1934. Soil Sci. **37,** 29.

(*Received 12 December 1959*)

FIG. 1. Lowland Rain Forest.

FIG. 2. Thick carpet of worm casts produced during the rainy season.

J. A. R. BATES — PLATE I

FIG. 1. Worm casts from *Hippopera Nigeriae*.

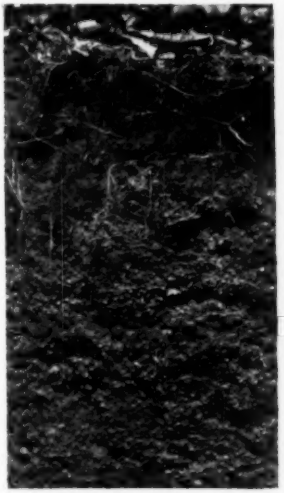

FIG. 2. The forest profile described. The gravel horizon in the upper part of the profile is the main feature of this series.

J. A. R. BATES — PLATE II

FIG. 1. A close-up of the structureless gravel horizon between 12 and 20 in. There are only traces of roots.

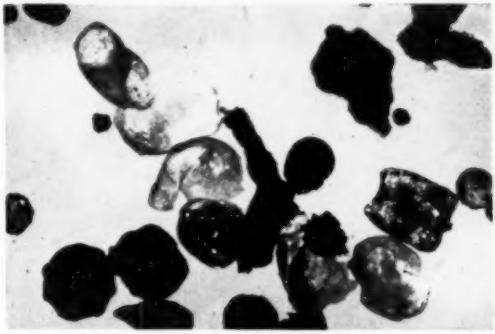

FIG. 2. Miscellaneous plant and animal matter debris in 0–4 in. layer. (Magnification approx. ×25.)

J. A. R. BATES — PLATE III

STUDIES ON A NIGERIAN FOREST SOIL

II. THE DISTRIBUTION OF PHOSPHORUS IN THE PROFILE AND IN VARIOUS SOIL FRACTIONS

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Summary

The distribution of total, total organic, total inorganic, and extractable phosphorus was determined for samples from a Nigerian forest profile, and for the sand fractions and aggregate fractions of the fine earth. The soil P is accumulated in the surface soil. Below 2 in. there is a marked fall in total P, reflecting a large decrease in the amount of organic P. Thereafter the total P is fairly constant down the profile. The concentration of P in the iron concretions is considerably higher than in the surrounding fine earth. In the gravel horizon, 12–30 in., over 80 per cent. of the total P at this level is immobilized in the concretions.

Only the surface soil contains appreciable amounts of P soluble in acetic acid, Truog's reagent, and NH_4F. Below 2 in., the amount of P extractable by these reagents falls sharply. There is very little Ca-bound phosphate below 2 in. Considerable amounts of P are extracted from all horizons by 0·1 N NaOH which extracts strongly adsorbed forms of P. The clay fraction of the topsoil contains large amounts of P soluble in NaOH.

Introduction

THERE are few data available on the total amount of phosphorus in typical West African soils, or the forms in which it is distributed. Values obtained for readily soluble phosphorus by several methods have nearly always been low. Doyne *et al.* (1938), extracting with a solution of potassium dihydrogen sulphate at pH 2, obtained an average of 10 p.p.m. P for the topsoils of thirteen Nigerian forest profiles, and 5 p.p.m. P for the topsoils of nine savannah profiles. Hardy and Amoroso-Centeno (1938), using the Truog (1930) method of extraction with 0·002 N sulphuric acid, found an average of 11 p.p.m. P in the top 6 in. of forty Gold Coast cocoa soils; de Endredy and Montgomery (1954), using the same extractant, found an average of 14·5 p.p.m. P in the first horizon (mean 0–2·7 in.), and 3·0 p.p.m. P in the second horizon (mean 2·7–8·3 in.) of fifty-one Gold Coast forest profiles. Nye (1950), using Bray's (1945) rapid-extraction procedure with 0·1 N hydrochloric acid and 0·03 N ammonium fluoride, found an average of 5 p.p.m. P in the 0–6-in. layers of eleven undisturbed forest sites. More recently Nye and Bertheux (1957) have examined the amounts and distribution of phosphorus in the top 6 in. of a range of Gold Coast soils, as well as the distribution in profile samples. They found that in thoroughly leached profiles in forest and savannah areas, acetic-acid-soluble phosphorus was low in the topsoil and decreased rapidly to trace values below 12 in. This trend has been found by many workers using different dilute aqueous extractants; for example, Middleton (1954) in the Sudan using Truog's reagent,

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Kellog and Davol (1949) in the Belgian Congo, Almeida and de Miranda (1954) in Angola using dilute acetic acid, and Tkatchenko (1954) in the Ivory Coast using 2 per cent. citric acid. The importance of this accumulation of 'available' phosphorus in the surface horizon is frequently emphasized.

Only Nye and Bertheux (1957) have investigated the distribution of phosphorus in various particle-size fractions in tropical soils. They also estimated the phosphorus content of the iron concretions frequently found in tropical soils.

This paper presents the data obtained from an investigation into the amounts and the distribution of total and 'extractable' phosphorus in the forest profile described in Part I (Bates, 1960). The phosphorus in the various soil fractions, obtained by the method of separation in Part I, and in the pisolitic iron concretions was also measured.

Experimental

Total phosphorus was determined by Sherman's (1942) method, which involves digestion with 60 per cent. perchloric acid and colorimetric estimation of the phosphorus in the filtrate. Organic phosphorus was measured as the increase in inorganic phosphorus extracted by 0·2 N sulphuric acid, after ignition at 550° C. for one hour (Saunders and Williams, 1955). Total inorganic phosphorus was obtained by the difference between total phosphorus and total organic phosphorus.

Easily extractable phosphorus was measured by the following methods. Acetic-acid-soluble phosphorus was determined by a one-hour extraction with 0·5 N acetic acid, with an extractant:soil ratio of 50:1. Truog's reagent, 0·002 N sulphuric acid, pH 3, was also used. Adsorbed phosphorus was extracted by the method of Bray and Kurtz (1945) using 0·5 N ammonium fluoride, pH 7·0, extractant:soil ratio 50:1. Phosphorus was also determined by digestion with 0·1 N sodium hydroxide for one hour. Saunder (1956) proposed this method for the extraction of available phosphorus from tropical soils, particularly red earths, where the phosphorus is present in strongly adsorbed forms.

All phosphorus contents were measured colorimetrically. In the total phosphorus determination the phosphovanadomolybdate method was used (Kitson and Mellon, 1944) and in all other cases the molybdenum-blue method (Dickman and Bray, 1940).

Discussion of Results

Profile

The parent quartzose rocks of the forest soils of West Africa are not particularly deficient in phosphorus. Junner and James (1947) give values for fifteen samples from Ghana with an average of 700 p.p.m. P, which is only a little below the general average of 870 p.p.m. for granite (Goldschmidt, 1954).

In the forest soil studied the total phosphorus is high throughout the profile, especially in the topsoil which contained 553 p.p.m. P in the 0–2-in. layer (see Table 1).

This surface accumulation of total phosphorus has been reported by

TABLE 1

Phosphorus in the Fine-earth Fraction of the Profile and in the Concretions

	Worm casts	0–2″	2–7″	7–12″	12–20″	20–30″	40–50″	60–72″
Total P in fine earth, p.p.m.	603	553	210	283	275	230	252	260
Organic P in fine earth, p.p.m.	450	405	95	70	45	42	50	103
Total P in concretions, p.p.m.	..	718	715	665	563	570	510	358
P in concretions as a % of total P in profile sample	..	2	45	71	85	82	63	15
Carbon/organic P ratio	153	115	44	43	40	50	42	(5)

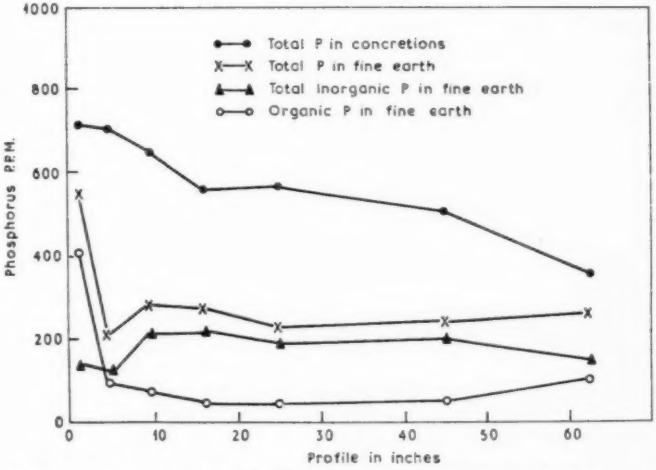

FIG. 1. Total, organic, and total inorganic phosphorus in the fine-earth fraction, and phosphorus content of the concretions.

many authors including Ghani and Aleem (1943) working on Indian forest profiles, and by Nye and Bertheux (1957) in Ghana. It has been attributed to the action of vegetation in transferring phosphorus from the root zone to the surface litter.

The decomposition of this litter is confined to the top 2 in., and the bulk of the fine feeding roots are to be found in the surface soil; thus most of the phosphorus appears to be in a closed cycle. The phosphorus compounds leached through the profile may be balanced by the small uptake of phosphorus from the lower parts of the profile by deep-rooted plants. The 2–7-in. layer contained least total phosphorus in the profile. This may be due in part to removal by vegetation, but also to the fact that it is near the approximate lower limit of worm activity. The high level of

total phosphorus in the surface soil is a reflection of the very high amount of organic phosphorus. There is over 400 p.p.m. in this layer, 75 per cent. of the total phosphorus in the fine earth. The marked fall in organic phosphorus below 2 inches results in a fall of total phosphorus in the same horizon.

The variations of total and organic phosphorus down the profile are shown in Fig. 1.

Below 7 in. the total phosphorus in the fine earth is fairly constant, varying betwen 230 and 283 p.p.m. Below 7 in. the organic phosphorus decreases steadily to about 30 in., but there is an increase to 100 p.p.m. at 60–72 in. The carbon/organic-phosphorus ratio is high in worm casts and the topsoil, but drops to 44 just below the surface soil, and is fairly constant thereafter. A sample of decaying litter collected from the soil surface contained 900 p.p.m. total P, of which 697 p.p.m. were organic.

Phosphorus content of iron concretions in the profile

In the mechanical analysis of samples from the profile, all particles larger than 1 mm. were termed gravel. This gravel consisted of a mixture of quartz gravel and iron-oxide concretions (with some manganese concretions at the lower levels). These iron concretions are rich in phosphorus which, since the concretions are relatively stable (Nye, 1955) under the existing conditions of weathering, is effectively locked up and unavailable to the plant. The concretions were removed by hand from the quartz gravel and samples were ground to a fine powder. The pisolitic iron concretions are frequently hard, whereas the manganese concretions are much softer. The total phosphorus content of the concretions from various levels of the profile is given in Table 1.

At all levels the concentration of phosphorus in the concretions is appreciably higher than in the surrounding fine earth. Below 12 in., the ratio is about 2:1. In the very gravelly layer from about 12 to 30 in., over 80 per cent. of the total phosphorus in the soil is in the concretions. The abundance of concretions varies considerably in tropical soils, from complete absence of concretions to a massive iron-oxide hardpan many feet thick, thus generalization about the percentage of the total phosphorus locked up in this way is impossible. Where large numbers of concretions occur in a gravel layer, high percentages of the total soil phosphorus can be immobilized in them.

'Extractable' or 'available' phosphorus in the profile

'Extractable' phosphorus was determined in profile samples, using the four extractants described above, and the results obtained are summarized in Table 2. These figures show that only the worm casts and the 0–2-in. layer contain any appreciable amount of phosphorus soluble in acetic acid, Truog's reagent, and ammonium fluoride. For these three reagents the values obtained fall sharply below 2 in. This agrees with the results of the workers mentioned earlier.

According to Williams and Saunders (1956) both acetic acid and Truog's

reagent extract the following forms of phosphate—water-soluble phosphates, calcium phosphates, hydroxy- and carbonate apatites, magnesium and manganese phosphates, and some chloro- and fluoro-apatites. Extraction by acetic acid is affected by fixation of the extracted phosphate by iron and aluminium compounds. The use of the fluoride ion, a powerful

TABLE 2

'Extractable' Phosphorus in Profile Fine Earth

p.p.m. P extracted by	*Worm casts*	0–2″	2–7″	7–12″	12–20″	20–30″
Acetic acid . .	32	24	2·1	0·9	1·3	0·4
Truog's reagent, pH 3·0	32	29	1·5	1·7	1·2	1·2
NH_4F, pH 7·0 . .	46	33	1·8	3·6	2·1	1·6
0·1 N NaOH . .	74	34	19	33	32	35

replacer of adsorbed phosphate, as extracting reagent, results in a slight increase in extracted phosphate over the acid extractants, but this also shows the very sharp decrease below 2 in. This rapid decrease is due to the concentration of soluble and readily mineralizable phosphorus on the surface in the litter. The pH is highest in the worm casts and the 0–2-in. layer, and it is known that the acid-soluble phosphorus increases with the pH. The alkali-soluble fraction of the soil phosphorus is almost constant down the profile, except in the worm casts and the 2–7-in. layer. Sodium hydroxide extracts the anionically adsorbed phosphates, and basic iron and aluminium phosphates as well as organic phosphorus. (Only the inorganic phosphorus is determined here since the organic phosphorus is estimated by ignition and acid extraction.)

Two factors probably contribute to the low values in the 2–7-in. layer. There is movement of iron-oxide-rich clay in both directions, upwards due to worm and termite activity, and downwards due to illuviation, and one would expect this horizon to be low in silt and clay for these reasons.

The Distribution of Phosphorus in Different Particle-size Fractions of the Fine Earth

Profile

The fractions investigated were coarse sand, fine sand and aggregate fractions, coarse silt, silt, and clay as defined in a previous paper (Bates, 1960). The total phosphorus present in the fractions at different profile levels is shown in Table 3.

At all depths, the concentration of phosphorus in the mineral sand fractions is less than in the aggregated silts and clay, although the differences decrease with depth. The phosphorus content of the coarse-sand fraction generally increases with depth. This is due to the fact that although the iron oxide concretions, rich in phosphorus, are concentrated in the gravel fraction, some small concretions occur in the coarse sand fraction and the proportion of these increases with depth. The fine-sand

fraction does not contain concretions, and has a reasonably constant phosphorus content down to 30 in. In spite of the low concentration of phosphorus in the mineral sands, the contribution of these fractions to total phosphorus, although low in the surface soil, reaches over

TABLE 3

Total Phosphorus (p.p.m.) in Aggregate Fractions down the Profile

	Worm casts	0–2″	2–7″	7–12″	12–20″	20–30″
Total fine earth . .	603	553	210	283	275	230
Coarse sand . .	90	70	58	125	138	170
Fine sand . . .	235	235	168	240	245	240
Coarse silt . . .	1,085	1,040	453	338	330	270
Silt	1,395	1,400	708	418	335	268
Clay	1,620	1,680	895	430	415	300

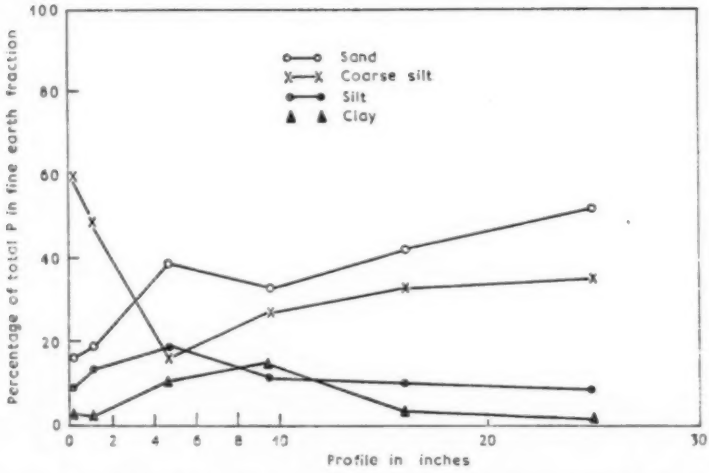

FIG. 2. Phosphorus in sand, coarse silt, silt, and clay as percentage of the total phosphorus in the fine-earth fraction.

50 per cent. at 30 in. because of the high percentage of coarse and fine sand relative to combined silts and clay.

The recovery of phosphorus on fractionating the fine earth was between 83 and 95 per cent., and no account was taken of water-soluble phosphorus lost in the fractionation. This would be highest for the surface soils. Approximately 3 per cent. of total phosphorus in the 0–2-in. layer was found in plant residues separated.

The silts and clay in the worm casts and 0–2-in. layer are particularly rich in phosphorus, the larger part of it being organic phosphorus (see Table 4). The sharp drop in total phosphorus in the fine earth below

2 in. is now seen to be due to the decrease in phosphorus content of the finer-sized particles. At 30 in. the phosphorus contents of fine sand, coarse silt, silt, and clay are about the same, and not much higher than that of the coarse sand.

TABLE 4

Organic Phosphorus in Sands and Aggregate Fractions

	Coarse sand		*Fine sand*		*Coarse silt*		*Silt*		*Clay*	
	Org. P p.p.m.	*As % of total P in fraction*	*Org. P p.p.m.*	*As % of total P in fraction*	*Org. P p.p.m.*	*As % of total P in fraction*	*Org. P p.p.m.*	*As % of total P in fraction*	*Org. P p.p.m.*	*As % of total P in fraction*
Worm casts	10	11	30	13	672	62	952	68	914	56
0–2″ .	14	19	48	20	785	75	1,110	79	1,052	65
2–7″ .	10	17	19	11	248	55	454	64	428	48
7–12″ .	13	10	15	6	106	31	151	36	154	36
12–20″ .	9	6	10	4	91	28	98	29	53	13
20–30″ .	22	13	24	10	84	31	75	28	—	—

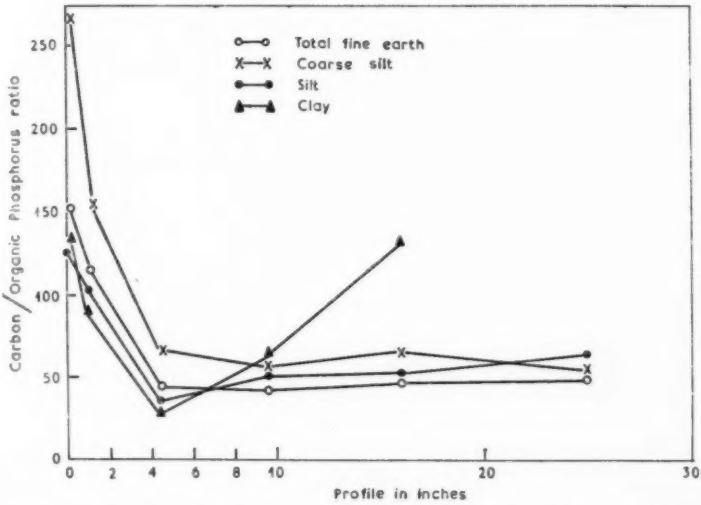

FIG. 3. Carbon/organic-phosphorus ratio for total fine earth, coarse silt, silt, and clay in the profile.

The organic phosphorus in the sands separated from all levels is low and probably occurs in organic material adsorbed on, or retained by, the sands as a surface coating. Microscopic examination of the sand particles shows deposits of humic material in the cracks and fissures of individual sand grains. In the topsoil the silt and clay are appreciably richer in organic phosphorus than the coarse silt, which contains aggregates of the finer-sized particles. The carbon/organic-phosphorus ratio is higher for coarse silt than silt and clay (Fig. 3).

'Extractable' Phosphorus in Particle-size Aggregate Fractions of the 0–4-in. Level

The particle-size aggregate fractions of the 0–4-in. sample of the profile taken for examination of organic matter were extracted by the four reagents used previously to characterize phosphorus in the profile. The amounts extracted from the sands by all four reagents are low, the most efficient extractant being sodium hydroxide (Table 5): the sands thus

TABLE 5

'Extractable' Phosphorus in Particle-size Fractions of the 0–4-in. Level

p.p.m. P soluble in	*Coarse plant residues*	*Fine plant residues*	*Coarse sand*	*Fine sand*	*Coarse silt*	*Silt*	*Clay*	*Total soil 0–4 in.*
0·5 N acetic acid .	109	141	3	5	50	49	15	12
Truog's reagent .	56	86	2	4	65	74	27	13
NH_4F . . .	47	51	5	9	51	68	89	15
0·1 N NaOH . .	86	96	12	10	62	82	251	25

contain very little calcium-bound phosphorus. Plant residues are highest in acetic-acid-soluble phosphorus, but the other reagents also extract considerable amounts. All four reagents remove comparable amounts from the coarse-silt and silt fractions, the variation being greatest for the silt. The clay fraction shows an interesting trend—the 'extractable' phosphorus increasing rapidly with the pH of the extracting solution. The acetic-acid-soluble phosphorus is 15 p.p.m., while 0·1 N sodium hydroxide extracts 251 p.p.m.

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REFERENCES

ALMEIDA, L. A. V., and DE MIRANDA, V. H. B. 1954. Trans. 5th Int. Congr. Soil Sci. **3**, 263.
BATES, J. A. R. 1960. J. Soil Sci. **11**, 246–56.
BRAY, R. H., and KURTZ, L. T. 1945. Soil Sci. **59**, 39.
DE ENDREDY, A. S., and MONTGOMERY, C. W. 1954. Trans. 5th Int. Congr. Soil Sci. **3**, 268.
DICKMAN, S. R., and BRAY, R. H. 1940. Indust. Engng. Chem., Anal. Ed. **12**, 665.
DOYNE, H. C., HARTLEY, K. T., and WATSON, W. A. 1938. 3rd W. Afr. Agric. Conf., 227.
GHANI, M. O., and ALEEM, S. A. 1943. Indian J. Agric. Sci. **13**, 337.
GOLDSCHMIDT, V. M. 1954. Geochemistry. Oxford University Press.
HARDY, F., and AMOROSO-CENTENO, E. H. 1938. Imp. Coll. Trop. Agric. Trin. 7th Ann. Rep. Cacao Res. 1937.
JUNNER, N. R., and JAMES, W. J. 1947. Gold Coast Geol. Surv. Bull. No. 15.
KELLOGG, C. E., and DAVOL, F. D. 1949. I.N.E.A.C. Ser. Sci. No. 46.
KITSON, R. E., and MELLON, M. G. 1944. Indust. Engng. Chem., Anal. Ed. **16**, 379.
MIDDLETON, K. R. 1954. Trans. 5th Int. Congr. Soil Sci. **3**, 218.

NYE, P. H. 1950. Trans. 4th Int. Congr. Soil Sci. **1**, 246.
—— 1955. J. Soil Sci. **6**, 73.
—— and BERTHEUX, M. H. 1957. J. Agric. Sci. **49**, 141.
SAUNDER, D. H. 1956. Soil Sci. **82**, 457.
SAUNDERS, W. M. H., and WILLIAMS, E. G. 1955. J. Soil Sci. **6**, 254.
SHERMAN, M. S. 1942. Indust. Engng. Chem., Anal. Ed. **14**, 182.
TKATCHENKO, B. 1954. Centre Rech. Agron. Bingerville, Bull. Sci. No. 5, 261.
TRUOG, E. G. 1930. J. Amer. Soc. Agron. **22**, 874.
WILLIAMS, E. G., and SAUNDERS, W. M. H. 1956. J. Soil Sci. **7**, 90.
——— 1956. Ibid. **7**, 189.

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SOIL–FOREST TYPES OF THE YUKON AND TANANA VALLEYS IN SUBARCTIC ALASKA[1]

S. A. WILDE AND H. H. KRAUSE[2]

WITH 1 PLATE

Summary

The region consists of flood plains, river terraces, low mountains, and dissected plateaux. Much of the area is covered with wind-blown, micaceous silt and fine sand. The summer temperature of nearly 100° F. drops in winter to −70°. The mean annual precipitation is about 12 in. The important types of forest soils include lithosols and regosols, alluvial soils, melanized raw-humus soils, micropodzols, half-bog soils, lowmoor peat, highmoor bog soils, and tundra-forest soils. Forest cover consists of white and black spruce, tamarack, paper birch, aspen, and tacamahaca poplar, accompanied by Sitka alder, willows, Alaska rose, highbush cranberry, many heath shrubs of both American and Eurasian origin, mosses (largely of *Sphagnum* and *Hylocomium* genera), and lichens.

Spruce stands on productive loessial uplands and permafrost-free terraces yield as much as 15 Mbf. per acre. A comparatively rapid growth of trees on lithosols and regosols, attaining 0·3 cords per acre per year, is attributed to large differences between the day and night temperatures resulting in condensation of water on fissures and fragments of rocks. Highmoors, covering slopes up to 45°, and some half-bog soils support sporadic cover of dwarfed trees; these otherwise unproductive sites provide food and shelter for wildlife, an important item in Alaska's economy.

The immediate neighbourhood of highmoor peat and alkali solonchak soils, as well as the development of non-podzolic, melanized soils covered with thick raw humus, are among many paradoxes of the Alaskan environment.

THE valley-plateau complex of interior Alaska is delineated on the north by two closely coinciding boundaries: the Brooks Range and the Arctic Circle. The southern boundary is formed by the towering Alaska Range. On the west the forests of the region grade into a mosaic of dwarfed spruce, peat bogs, and lakes, a landscape which culminates in the swampy, treeless plain of the seashore and the Yukon-Kuskokwim Delta.

The basins of the two large Alaska rivers, the Yukon and the Tanana, consist of wide flood plains and a series of terraces. The plains are dotted with meandering streams, ponds, swamps, and marshes; the terraces are resting on thick beds of stratified gravel. The uplands are formed by low mountains, hills, foot slopes of the bordering ranges, and dissected plateaux. The region is underlain by permafrost and in a large part is covered with deposits of wind-blown silt and fine sand, predominantly of mica (Brooks, 1953).

Like most of Alaska, its central part is a land of extremes, contrasts, and paradoxes. The annual amplitude of temperature approaches

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170° F., from nearly 100° F. in summer to −70° F. in winter. Some areas are only a few scores of feet above sea level, whereas the neighbouring Mount McKinley, the highest point on the North American continent, exceeds 20,000 ft. The height increment of white spruce on loessial deposits may be contrasted with the growth of stunted black spruce, attaining less than 1 in. diameter at the age of 200 years. The wildlife population includes moose, grizzly bear, and brown bear, animals whose weight exceeds 1,000 lb., as well as the microscopic weasels, the world's tiniest members of the carnivorous mammals. The peculiarities of climate with its mere 12 in. of annual precipitation and the average growing-season temperature of 55° F. bring to the immediate neighbourhood deposits of highmoor peat and alkali solonchak soils, genetic types which are not usually found together. Soils covered by thick layers of peat-like raw humus, but exhibiting no differentiation into leached and accumulative horizons, are another paradox of the boreal environment. The continuity of forest distribution is often destroyed by fire, invasion of *Sphagnum*, irregular occurrence of permafrost, solifluxion, and especially the orientation of slopes (Krause *et al.*, 1959).

The information reported in this paper is based on a cursory examination of soils and forest stands on about 200 areas, and a detailed analysis of soil properties, forest composition, and the rate of forest growth on 37 sample plots. The plots were selected among the representative examples of soils and forest cover. In spite of considerable diversity of landscape, the establishment of the general relationships was greatly facilitated by the fact that soils and forest vegetation in interior Alaska form a limited number of units, all of which exhibit sharply pronounced biocenotic characteristics. The morphology of the principal forest soils of interior Alaska is illustrated schematically in Fig. 1.

Previous investigations of soils and forest ecology, particularly those of Kellogg and Nygard (1951) and Lutz (1956), served as valuable guides to the authors in their journey on unfamiliar trails. This study owes much to the wholehearted co-operation of Dr. Allan H. Mick, Director of the Alaska Agricultural Experiment Station, Dr. Samuel Rieger, Territorial Soil Scientist, U.S. Department of Agriculture, and Drs. F. C. Dean and A. W. Johnson of the University of Alaska.

Skeletal soils (Lithosols and Regosols). The erosive action of wind, water, and glaciers has benefited the productive potential of land in subarctic Alaska to an extent unparalleled in other parts of the world. The forces of denudation endowed this territory with a very large area of loess-like deposits and river terraces, having nutrient-enriched, stone-free substrata of favourable texture, and often either level or smooth topography.

Except for the transported aeolian and alluvial mantles, the surface geologic formations of interior Alaska are characterized by greatly retarded processes of weathering and a wide occurrence of rock outcrops and debris of stones and gravel. In spite of their thinness and other unfavourable properties, these primitive soils are moderately productive; they support a considerable amount of pulpwood and even timber stands in the subarctic portion of the peninsula.

The conditions which make possible the existence of forest vegetation on slightly weathered substrata in this part of the world are three. First, the climatic peculiarities of Alaska, particularly the large differences between day and night temperatures during the growing season are responsible for the condensation of an appreciable supply of water on exposed surfaces of outcrops, rock fissures, and rock fragments. Next in importance is the nearly universal distribution of spruce species, trees

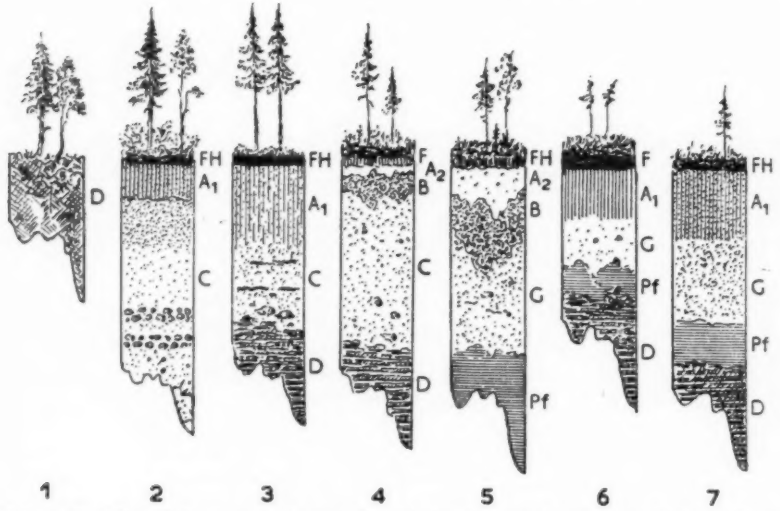

FIG. 1. Profiles of forest soils in interior Alaska (schematic presentation): 1, Rock outcrops; 2, Alluvial soil of river terraces; 3, Weakly melanized raw-humus soil formed on loess-like deposit over micaceous schist; 4, Micro-podzol developed on a similar parent material; 5, Gley-podzolic soil underlain by permafrost; 6, Highmoor peat; 7, Tundra-forest soil. (Frozen substratum is designated by the symbol Pf.)

whose root systems, armed with chelating compounds and mycorrhizal fungi, possess a very high capacity for extracting nutrients from unweathered minerals. Finally, most of the geologic formations are comprised of micaceous schists and other igneous rocks carrying a supply of nutrients adequate for coniferous trees.

The potentialities of forest growth on skeletal substrata are exemplified by the following description of white spruce on slightly weathered outcrops of andesite. The selected sample area of steep slopes and definitely unfavourable petrography illustrates the lower rather than the upper margin of timber production on these truly embryonic soils.

The ferro-magnesian lithosol, forming slopes of approximately 40°, is sporadically covered with an overwash of fine earth enriched in organic matter. The most advanced stages of soil formation are characterized by a cover of live mosses and by a 2–3-in. layer of dark brown amorphous humus overlying the slightly corroded rock. At the foot of the slope the

outcrops are covered by talus. The nature of humus-enriched debris is illustrated by the following analyses:

pH	*Tot.* N	*Avail.* P_2O_5	*Avail.* K_2O	*Exch.* Ca	*Exch.* Mg
5·9	0·91%	59·4 p.p.m.	417 p.p.m.	44·4 m.e./100 g.	5·64 m.e./100 g.

Forest cover consists of 70–140-year-old white spruce accompanied by many saplings and a few seedlings, some paper birch, tacamahaca poplar, Sitka alder, and highbush cranberry. The average height of dominant trees is 52 ft.; some of the old trees are 20 in. in diameter. The density of stand is 70 per cent. of the full stocking and the volume about 14 cords per acre of pulpwood, but only 5 Mbf. of saw logs. The average annual increment is about 0·2 cord per acre (Plate I*a*).

The intermittent ground cover consists of *Hylocomium splendens*, *Pleurozium schreberi*, *Polytrichum commune*, and *Dicranum fuscescens*, with a sprinkling of *Cornus canadensis*, *Vaccinium uliginosum*, *Geranium erianthum*, *and Carex* spp.

The rate of tree growth, the stability and density of stands, and the occurrence of natural regeneration increase in direct relation to the accumulation of weathered debris—gravel, sand, and fine-earth material. On rock outcrops mantled with gravelly detritus, or on regolith soils, the growth of spruce often exceeds 0·3 cord per acre per year.

These skeletal soils permit reasonably profitable exploitation only on long rotations, exceeding 100 years, and with minimum expenditure on forest management. The forest regeneration of clear-cut areas is an extremely slow and uncertain process which under present economic conditions cannot be accelerated by artificial reforestation. Therefore, the perpetuation of forest cover on these soils necessitates costly partial cuttings, removing not more than 30–40 per cent. of the stand's volume. In spite of all these shortcomings, the lithosols and regosols of Alaska cannot be neglected by the forester; they comprise a large part of the territory and produce an annual increment far exceeding that attained on the enormous area of moss-covered soils underlain by the permafrost.

Alluvial soils. The profiles of these water-laid, stream-bordering soils exhibit considerable variation imposed by the caprices of inundating waters. In most instances, however, the textural and petrographic differences between alluvial soils have little influence on the distribution and growth of forest vegetation because of the more powerful effects of the proximity of the ground-water table, the high content of bases, and the complete or partial liberation of soil from permafrost. These beneficial influences are reflected in a high rate of growth of practically all important tree species of the region, particularly white spruce (Plate I*b*). Even beyond the climatic boundary of forest distribution, trees follow alluvial soils for many miles into the tundra; one of the virgin stands of white spruce, with an average height of nearly 80 ft., is located on a stream bottom in the north-east corner of the peninsula, a few miles distant from the shore of the Beaufort Sea.

From the standpoint of practical forestry, valuable alluvial soils in

interior Alaska are largely confined to river terraces, particularly those of the Yukon and Tanana rivers. When commercial forestry comes to this region, it will be first confined to river terraces, for they present the most favourable conditions for planned forest management: high productive potential of the land, considerable continuous areas, level topography, stone-free soils, and natural avenues for timber extraction.

A picture of a productive soil of the Tanana River terrace is given by the following description of a virgin stand of white spruce near Thirty-Mile Slough.

The soil is the permafrost-free Nenana very fine sandy loam with the following profile:

S: 0–2 in.	Live *Hylocomium* and *Pleurozium* mosses.
F: 2–7 in.	Matted mycelial moss mor; brown, partly decomposed mosses and remains of trees, including fragments of orange-coloured wood; penetrated by roots and fungal mycelia.
A_1: 7–10 in.	Olive-brown (2·5 Y 4/4) to grey-brown (2·5 Y 5/2), friable silt loam with black lenses of decomposed organic matter up to 1 in. in diam.; high concentration of roots.
A_1C: 10–17 in.	Mixed grey (10 YR 6/1) and brown (7·5 YR 4/4) fine sandy loam, friable and crushing into subangular blocks; penetrated by roots and with few organic lenses.
C: 17–36 in.	Grey fine sand (10 YR 5/1) with some brown mottling, horizontal brownish veins, and a few roots; at 26 in. the texture changes to stratified coarse sand and gravel.

The results of soil analyses, using methods described by Wilde and Voigt (1959), are given in Table 1.

TABLE 1.

Content of Nutrients and Associated Fertility Factors in a Profile of Alluvial Fine Sandy Loam (Nenana Series). Thirty-Mile Slough, near Fairbanks

Horizon and depth (in.)	pH	*Tot.* N	*Tot.* C	C/N *ratio*	*Avail.* P_2O_5	*Avail.* K_2O	*Exch.* Ca	*Exch.* Mg
		%			*p.p.m.*		*m.e./100 g.*	
F: 2–7	4·5	1·12	43·1	38·5	85	1,172	32·6	5·0
A_1: 7–10	5·1	0·17	3·7	21·7	51	184	6·1	2·2
A_1C: 10–17	7·4	0·16	2·6	16·7	49	83	14·4	3·0
C: 17–36	7·9	0·02	—	—	29	77	12·2	0·7

Forest cover is white spruce, 100–210 years old, with intrusions of tamarack, tacamahaca poplar, and paper birch, and a sporadic understorey of Sitka alder and wild rose. The average height and diameter of trees are 82 ft. and 10 in. respectively. The stand is nearly fully stocked and the volume approaches 14 Mbf. per acre.

The composition of the lesser vegetation was appraised by the use of D/F quotients, where D is density or the number of specimens encountered per 100 linear ft. of a transect, and F is frequency of occurrence in per cent. of 10-ft. linear segments. The ground is covered by *Hylocomium*

splendens and *Pleurozium schreberi* mosses. The association of vascular plants is: *Vaccinium vitis idaea* 292/100, *Cornus canadensis* 84/100, *Lycopodium annotinum* 49/20, *Geocaulon lividum* 14/83, *Pyrola secunda* 19/37, *Vicia americana* 2/3, and occasional *Lupinus arcticus*, *Festuca altaica*, and *Carex bigelowii*.

The recorded characteristics of forest growth on soils of river terraces coincide closely with those found on alluvial deposits of the boreal zone of both Europe and Asia (Morozov, 1930; Mikhailov, 1956).

Within the boundaries of the region studied, alluvial lowlands occasionally include patches of alkali soils with a reaction approaching pH 9 and nearly 0·2 per cent. of water-soluble sodium (Wilde and Krause, 1959). These soils bear a strong resemblance to solonchak and solonetz soils formed under comparable climatic conditions in the Yakutsk province of Siberia (Glinka, 1927).

Melanized Raw-Humus soils (Subarctic Brown Forest Soils; Incipient Podzols). This soil group occupies an enormous total area in the forest-tundra belt of North America and Eurasia, and Russian pedologists recognized it as an independent soil group under the names of 'Latent Podzol', 'Crypto-Podzol', and 'Incipient Podzol' (Glinka, 1931; Filatov, 1945). In northern Europe and Siberia the boundaries have been gradually established with a fair degree of accuracy (Mikhailov, 1956). American soil scientists designated the boreal non-podzolic raw-humus soils as 'Subarctic Brown Forest Soils' (Kellogg and Nygard, 1951).

Considering either the morphology of these soils or the ecological relationships none of these terms is entirely satisfactory. Many of the upland soils in the tundra-forest transition have not been touched by the process of podzolization in the course of more than 20,000 years of their existence. The American term was suggested on the assumption that non-podzolic soils of boreal regions are similar to the brown forest soils of temperate regions. Neither in profile features, composition of native vegetation, state of fertility, nor adaptation to farm and forest crops have the boreal raw-humus soils anything in common with brown-earth and related mull soils of the temperate zone.

The presence of the raw-humus layer, varying in thickness from 3 to as much as 6 in., is of paramount practical importance, considering either silvicultural or agronomical aspects. On the other hand, the stability of iron and aluminium sesquioxides in the entire profile in spite of the presence of raw humus is a phenomenon not encountered in soils of any other region of the world. Because of this peculiarity, these soils occupy a unique, totally independent position in the world's family of soils. Their pattern of development cannot and should not be related to or, rather, confused with that of any other genetic soil groups.

Within the framework of available terminology, the objective and descriptive name for these amphigenic soils is *melanized raw-humus soils*. Depending on the amount of incorporated humus, strongly and weakly melanized varieties of these soils may be recognized. The latter variety is predominant in interior Alaska.

The productive capacity of the weakly melanized raw-humus soils under forest cover is illustrated by the following description of the

Fairbanks silt loam, located on the southwestern slope, 15 miles west of College in the Rosa Creek Forest Reserve.

S: 0–2 in. Live *Hylocomium* mosses.

FH: 2–6 in. Matted moss mor composed of the remains of mosses and spruce needles of a dark brown colour (10 YR 2/2), penetrated by abundant mycelia and rootlets; more or less humified in the lower inch of the horizon.

A_1: 6–10 in. Friable silt loam of a dark greyish-brown colour when moistened (10 YR 3/2 to 5/2); in dry condition the dark colour is not apparent and the profile resembles that of cryptorganic soils. The horizon exhibits fine platy structure and is penetrated by roots.

A_1C: 10–28 in. Brown silt loam (10 YR 4/3 to 4/2) of weak subangular blocky structure with faint clay skins on peds and a few coarse tree roots. The middle of the horizon is intersected by a 1/4-inch thick, nearly horizontal band of a dark brown silty clay loam, somewhat enriched in organic matter.

C: 28–34 in. Partly disintegrated micaceous schist resting on unweathered substratum.

The results of the profile analyses, given in Table 2, reveal that the soil has a fairly high supply of nutrients, concentrated largely in the

TABLE 2

Content of Nutrients and Associated Fertility Factors in a Profile of Weakly Melanized Raw-Humus Silt Loam (Fairbanks Series). Rosa Creek Forest Reserve

Horizon and depth (in.)	pH	Silt 0·05 to 0·002 mm.	Clay < 0·002 mm.	*Tot.* N	*Tot.* C	C/N *ratio*	*Avail.* P_2O_5	*Avail.* K_2O	*Exch.* Ca	*Exch.* Mg
		%		%			*p.p.m.*		*m.e./100 g.*	
FH: 2–6	6·2	—	—	1·37	34·55	25·1	308	1,400	62·5	11·3
A_1: 6–8	5·5	68·1	10·2	0·26	5·30	20·4	87	125	15·0	4·8
A_1: 8–14	5·1	68·0	10·8	0·09	1·88	19·8	23	59	4·8	2·9
A_1C: 14–20	5·2	70·6	11·6	0·04	0·71	16·5	5	47	3·6	2·5
Interlayer	5·6	61·5	20·4	0·06	1·01	16·5	15	92	7·3	7·4
C_1: 20–24	6·1	77·8	9·2	0·03	0·52	15·8	107	42	4·5	5·3
C_2: 24–28	6·8	73·6	3·2	0·02	0·35	14·0	183	37	3·9	4·6

organic layer and the A_1 horizon with infiltrated humus. The latter horizon exhibits an ideal balance of all major nutrient elements. The content of replaceable magnesium reflects the chemical composition of the soil parent material. The distribution of the total nitrogen in the entire soil profile is in sharp contrast to that observed in podzolized soils.

The unusual, and thus far enigmatic, feature of these soils is the presence of a narrow band at approximately 18 in. This may be formed in part by flocculation of iron-loaded humates discharged from the mor layer. Judging from the analytical results, the illuviation is largely confined to the mere physical translocation of the fine clay and organic suspensions without an appreciable impoverishment of the surface mineral layer in bases and nitrogen.

The low average annual temperature, precluding the complete breakdown of colloidal humus, the hydrolytic effect of melt waters, and the sparse precipitation which is insufficient for the removal of humate suspensions from the soil profile, appear to be conditions responsible for the formation of the bands. The formation of somewhat similar bands in soils of Siberia was attributed by some Russian pedologists to the 'intra-solum weathering'.

The forest cover is white spruce, 110–35 years old, of average diameter 12 in. and height 87 ft., with some paper birch, trembling aspen, and a scattering of Sitka alder. The yield at a density of 75 per cent. approaches 15 Mbf. per acre (Plate I*c*).

The ground cover is a nearly solid carpet of *Hylocomium splendens* with occasional *Hypnum crista-castrensis* and *Pleurozium schreberi*. The incidental occurrence of vascular plants is confined to *Viburnum edule*, *Geocaulon lividum*, *Mertensia paniculata*, and *Festuca altaica*.

The scarcity of herbaceous plants and the absence of natural spruce regeneration are characteristic of this soil-forest type. The poor regeneration of white spruce on these moss-covered soils casts doubt on the climax nature of this species in the subarctic environment. A wide opening of the canopy is likely to cause invasion by *Sphagnum* and black spruce, an association which would preclude the regeneration of white spruce.

Occasionally, melanized soils of uplands are replaced by soils exhibiting very narrow leached horizons and faintly pronounced accumulative layers. Because of the weak development of profiles and the presence of the thick raw humus, such soils cannot be identified either with true podzols or podzolic soils. In Russian writings, these products of an arid boreal environment are called 'micro-podzols' or 'dwarf podzols' (Filatov, 1945).

In spite of a diligent search, the authors did not find virgin forest stands on micro-podzols, or even second-growth stands that had not been damaged by fire during the past 80 years. Nevertheless, available information suggests that micro-podzols develop under the influence of a dense cover of heath plants and a thick layer of rhizogenous mor, formed largely by a network of lingonberry and bilberry roots.

The presence of abundant ground vegetation on micro-podzols suggests a reduced density of autochthonous stands, a partial replacement of white spruce by black spruce, and a slower rate of tree growth. The very fact that most of the forest stands on micro-podzols had been damaged by fire suggests the pre-existence of partly open stands with overhanging branches and inflammable ground vegetation.

Half-Bog soils (Gley-Podzols and Peat-Gley Soils). These lowland soils, typical products of the cold boreal environment, are conducive to a vigorous growth of mosses which in time eliminate all trees except the hardy black spruce and tamarack. The rate of tree growth on these soils depends on the stage of forest succession and the properties of the soil such as the content of nutrients, the depths of the insulating moss layer, and the position of the permafrost. Half-bog soils, like peat deposits, present a series of different links of the chain of succession and, under

conditions of intensive forest management, require separation into several sub-types (Huikari, 1952; Wilde *et al.*, 1954). The more productive sub-types are characterized by the predominance of *Hylocomium*, *Hypnum*, and *Pleurozium* mosses, and the occurrence of permafrost at a depth of 2½ ft. or more. Soils of this group support white and black spruce with some tamarack and tacamahaca poplar, yielding as much as 12 cords per acre at the age of 70 years (Plate I*d*). Less productive half-bog soils are covered largely with *Sphagnum* mosses, are underlain by permafrost at a depth of less than 2½ ft., and support unsaleable stands of black spruce with occasional tamarack.

With the advance of succession, and subsequent impoverishment of groundwater in electrolytes, increase in the thickness of the moss layer over 8 in., and appearance of *Sphagnum fuscum*, the half-bog soils become increasingly peaty.

An example of half-bog soils in the advanced stage of their development was located near the town of Buffalo Center, Alkan Highway. A description of the profile is:

S:0–1½ in.	Live *Hylocomium* mosses.
F:1½–5 in.	Slightly compressed remains of tree foliage and mosses, penetrated by roots and fungus mycelia.
H:5–7 in.	Dark brown, nearly black, amorphous, muck-like organic matter containing a slight admixture of mineral particles in the lower portion of the horizon.
A_1G:7–15 in.	Yellowish-brown to grey fine sandy loam or very fine sand of aeolian origin, with occasional, faintly pronounced mottling; penetrated by a few coarse roots.
G:15–36 in.	Mottled yellowish-brown coarse silt, saturated with water and underlain by permafrost.

The results of profile analyses are given in Table 3.

TABLE 3

Content of Nutrients and Associated Fertility Factors of a Gley-podzolic Soil. Vicinity of Buffalo Center, Alkan Highway

Horizon and depth (in.)	pH	*Tot.* N	*Tot.* C	C/N *ratio*	*Avail.* P_2O_5	*Avail.* K_2O	*Exch.* Ca	*Exch.* Mg
		%			*p.p.m.*		*m.e./100 g.*	
F:0–4	3·8	0·862	37·6	43·7	180	982	9·0	3·2
H:5–7	3·5	0·784	18·3	23·4	18	65	1·7	0·7
A_2G:7–15	4·9	0·089	1·46	16·5	8	50	5·6	3·4
G:24–32	5·6	0·030	0·35	11·7	159	97	5·5	3·9

Forest cover is a mixed stand of black and white spruce, exhibiting a group distribution pattern. Approximate average age is 110 years. The largest stems of white spruce are 47 ft. high; the average diameter is 7 in. Black spruce attains a maximum height of 38 ft. and a diameter of 4½ in. The stand is accompanied by a scattering of tacamahaca poplar, 50–70 years old and 8–10 in. in diameter. All poplar trees examined were

infected with heart rot and exhibited a large percentage of dead branches. The volume of saleable timber is about 10 cords per acre. The understorey is Sitka alder and many clumps of spruce layering.

The ground cover includes a variety of mosses of patchy distribution: *Hylocomium splendens*, *Pleurozium schreberi*, *Polytrichum commune*, *P. strictum*, *Dicranum fuscescens*, *Paludella squarrosa*, *Aulocomnium palustre*, and occasionally species of *Sphagnum*. The moss layer supports a dense stand of low shrubs and forbs: *Vaccinium vitis-idaea* 344/100, *V. uliginosum* 23/50, *Empetrum nigrum* 89/70, *Ledum decumbens* with occasional *Ledum palustre* 21/55, *Equisetum sylvaticum* 10/55, *Pyrola grandiflora* 9/45, *Cornus canadensis* 7/45, *Rosa acicularis* 7/40, *Geocaulon lividum* 6/35, *Carex bigelowii* 16/30, *Andromeda polyfolia* 3/10, and *Arctostaphylos alpina* 6/15. A survey of the entire area revealed an incidental presence of *Calamagrostis canadensis*, *Pedicularis labradorica*, *Linnaea borealis*, *Petasites frigidus*, *Marchantia polymorpha*, and *Pyrola secunda*. The scattering of lichens included *Cladonia rangiferina*, *C. sylvatica*, *C. alpestris*, *Peltigera aphthosa*, *Cetraria islandica*, and *Nephroma arcticum*. One corner of the stand had hummocks of *Sphagnum capillaceum*.

TABLE 4

Composition of a Half-bog Loam Underlain by Permafrost at a shallow Depth and Including a Humus-enriched Gley Horizon. Alcan Highway near Big Delta

Horizon	*Depth (in.)*	pH	*Tot.* N %	*Tot.* C %	C/N *ratio*	*Avail.* P_2O_5 *p.p.m.*	*Avail.* K_2O *p.p.m.*	*Exch.* Ca *m.e./100 g.*	*Exch.* Mg *m.e./100 g.*
F	0–2	4·2	0·958	36·3	37·9	92·0	737	40·25	9·71
H_1	2–5	4·4	0·843	32·9	39·1	65·6	372	32·50	13·16
H_2	5–8	5·3	0·847	22·4	26·5	22·0	117	57·60	12·46
A_2G	8–15	6·9	0·051	0·82	16·1	115·0	120	16·20	3·01
A_1G	15–17	6·4	0·411	9·90	23·1	25·2	60	48·60	7·25
G	17–23	6·4	0·043	0·78	18·1	146·5	30	4·70	0·68

Occasionally, half-bog permafrost soils include within the gley horizon a black interlayer enriched in organic matter and bivalent bases. Results of analyses of such a profile are given in Table 4. Filatov (1945, p. 172) designated these secondary humus horizons by the symbol A_z and attributed their genesis to the presence of an interlayer of calcareous material.

Highmoor Peat (Raised-Bog Soils). The classification of this type is determined by the topographic location and the mode of development, rather than the profile morphology which at times is nearly identical with that of half-bog soils of the lowlands.

In the environment of subarctic Alaska, highmoors are formed at a wide range of altitude and not only on elevated plateaux and gentle slopes, but also on slopes approaching 45°, especially of northern and eastern exposures. There is evidence that the invasion of *Sphagnum* mosses often follows removal or heavy thinning of forest stands. To prevent the

conversion of productive lands into highmoors may be one of the most important tasks of regional soil conservation and forest management.

One of the profiles of the fully developed highmoor peat is located on a 35° slope of northern exposure, about 20 miles west of Fairbanks. The initial investigation of this deposit by Krause, Rieger, and Wilde (1959) revealed some profile features seldom encountered in similar soils of the world:

S: 0–3 in.	Live *Sphagnum* mosses.
F: 3–13 in.	Peat-like layer of slightly decomposed, compressed, yellowish-green remains of *Sphagnum*, penetrated by a few mycelia and many roots.
A_1G: 13–17 in.	Very dark, grey-brown (2·5 Y 3/2) micaceous silt loam with lenses and pockets of black (N 2/0) amorphous organic matter and few roots. Frozen in the lower part, but in spite of this containing some *Enchytraeidae*, pale-coloured 'ice worms', and many unidentified beetles resembling in size and appearance *Ips lineatus*.
G: 17–23 in.	Olive-grey (5 Y 4/2) micaceous silt loam with distinct olive-brown mottling and black streaks; penetrated by few roots. Frozen. Depth to the underlying schist substratum is approximately 30 in.

The forest cover on this soil is made up of black spruce, 115–30 years old (Plate I*e*) having an average diameter of 2·9 in., the average height of the tallest trees being 23 ft. The volume at 50 per cent. density is between 3 and 4 cords per acre. The stand also contains scattered Sitka alder (*Alnus sinuata*), bog birch (*Betula glandulosa*), willows (mostly *Salix glauca*), and spirea (*Spirea beauverdiana*).

The surface layer consists predominantly of *Sphagnum* spp., including *S. girgensohnii*, *S. compactum*, and *S. fuscum*, and occasional patches of *Polytrichum commune* and *P. strictum*. The moss cover is dotted with lichens, *Cladonia sylvatica*, *C. rangiferina*, *Cetraria islandica*, and *Peltigera aphthosa*. The association of vascular plants is made up of *Vaccinium vitis-idaea* (241/100), *V. uliginosum* (13/20), *Ledum decumbens* and *L. palustre* (74/100), *Rubus chamaemorus* (40/85), and *Eriophorum vaginatum* (12/25).

The deplorable condition of forest on this soil type is largely due to the insulating effect of *Sphagnum* which preserves the high level of the permafrost. From a strictly silvicultural viewpoint, therefore, one may agree with the opinion of some Finnish foresters that the *Sphagnum*, to be good, must be not only dead, but cremated. A similar conclusion in a different wording was reached by Lutz (1956).

While unproductive agriculturally or silviculturally, highmoors provide food and habitat for much wild life, as well as abundant marketable crops of lingonberries, bilberries, and cloudberries.

Lowmoor Peat (Bog-Moss Peat). Examination of peat deposits in the unglaciated interior of Alaska is likely to bewilder a specialist familiar with the orderly profile morphology of organic soils developed in regions of recent glaciation. The muskegs of the Tanana Valley usually present a sequence of organic layers belonging to distant geologic periods. As reported by Dachnowski-Stokes (1941), many deep peat deposits include

four superimposed muskegs. Some of the interlayers contain volcanic ash and loessial material. The composition of the lower strata is guarded from any alterations by the armour of ice, which in some instances is scores of millennia old. Ecologically, muskegs of interior Alaska are nearly exact copies of those found in Ontario or in the Lake States. A description of a representative bog moss peat, near the town of College, follows:

S: 0–4 in.	Live bog moss; pH 3·9.
P: 4–32 in.	Yellowish-brown, fibrous and spongy remains of *Sphagnum* with occasional admixture of *Polytrichum* and fragments of trees and heath shrubs; penetrated by roots in the surface 10 in.; compacted and including some rhizomes of sedges in the lower part. Reaction from pH 4·3 to pH 4·7.
M: 32–38 in.	Muck-like dark brown remains of wood of trees and heath shrubs, enriched in mineral particles, pH 5·7. Frozen below the depth of 34 in.

Forest cover consists of black spruce and tamarack, including seedlings, layering, saplings, and trees over 100 years old. The volume at the density of 60 per cent. is 5 cords per acre. The sporadic understorey includes *Betula glandulosa*, *Salix pulchra*, and occasional *Spiraea beauverdiana*.

The hummocky surface of the bog is formed by *Sphagnum girgensohnii*, *S. compactum*, *S. subsecundum*, *S. rubrum*, *S. fuscum*, *S. capillaceum*, and *Polytrichum strictum* with a sprinkling of *Cladonia*, *Cetraria*, and *Peltigera* lichens. The composition of the vascular plants is exemplified by the following results of a transect analysis: *Vaccinium vitis-idaea* 51/100, *V. uliginosum* 17/95, *Rubus chamaemorus* 35/85, *Andromeda polyfolia* 16/60, *Chamaedaphne calyculata* 7/10, *Ledum decumbens* 51/100, *L. groenlandicum* 3/10, *Drosera rotundifolia* 3/15, *Eriophorum vaginatum* 37/100, *Oxycoccus palustre* (*microcarpus*) 54/70, *Arctostaphylos alpina* 5/15, *Epilobium palustre* 3/10, some *Carex* spp., including *C. bigelowii*, and occasional *Empetrum nigrum*.

In spite of the widespread abundance of *Sphagnum*, the Tanana watershed has a surprisingly small total area of deep peat deposits, partly because of the youth of the surface geologic formation.

Tundra-forest soils. Within the region of interior Alaska, the boundary between the treeless tundra and the tundra-forest ecotone coincides closely with the isotherm of 50° F. for the growing season, that is from the end of May to the middle of August. With very few exceptions, tundra and tundra-forest soils are synonymous with permafrost soils.

Superficially, the physiognomy of the tundra-forest resembles that of European 'heath', a similarity largely imparted by the insulating effect of the thick layer of peat-like raw humus. A representative area of the tundra-forest transition was studied in detail on the northern slope of the Alaska range near Donnelly (Plate I*f*). The shallow soil exhibits a well-differentiated profile:

FH: 0–5 in.	A dark brown spongy mor layer derived largely from mosses and lichens; amorphous in the lower part.

A_1: 5–7 in. Dark brown sandy loam with a very high content of incorporated organic matter.

C: 7–12 in. Light brown gravelly sandy loam with faintly pronounced mottling; frozen in the lower part and underlain by micaceous schist.

Results of the profile analyses are given in Table 5.

TABLE 5

Composition of Tundra-forest Sandy Loam Supporting a Scattering of Black Spruce. Northern Slope of the Alaska Range near Donnelly

Horizon	*Depth (in.)*	pH	*Tot.* N	*Tot.* C	C/N *ratio*	*Avail.* P_2O_5	*Avail.* K_2O	*Exch.* Ca	*Exch.* Mg
			%			*p.p.m.*		*m.e./100 g.*	
FH	0–5	4·6	0·830	28·90	34·8	59·6	576	9·90	2·77
A_1	5–7	4·8	0·515	11·90	23·1	237·8	108	7·30	1·34
C	7–12	5·3	0·078	1·38	17·6	4·1	25	2·15	0·43

The forest cover is a thin scattering of black spruce with occasional thickets of bog birch, Sitka alder, and willows. The trees older than 100 years attain a maximum height of 15 ft. and diameter of $2\frac{1}{2}$ in. The surface layer presents a carpet of *Hylocomium splendens*, *Pleurozium schreberi*, *Polytrichum strictum*, *Dicranum fuscescens*, and *Aulocomnium turgidum*. The vascular vegetation is composed of *Vaccinium vitis-idaea* 67/100, *V. uliginosum* 24/100, *Empetrum nigrum* 61/100, *Ledum decumbens* 14/60, *Cornus canadensis* 15/40, *Linnaea borealis* 8/15, *Geocaulon lividum* 3/10, *Arctostophylos alpina* 9/15, *A. uva-ursi* 3/5, *Pyrola secunda* 7/10, *P. minor* 2/5, and *Antennaria monocephala* 2/10. The ground cover is accompanied by *Cladonia alpestris*, *C. rangiferina*, *C. sylvestris*, *Cetraria sylvatica*, *C. islandica*, *Alectoria ochroleuca*, and *Peltigera aphthosa*. The scattering of grasses includes *Poa arctica*, *Artemisia arctica*, *Festuca altaica*, and *Calamagrostis canadensis*.

This type has little silvicultural importance; it represents the last outpost of the forest in its battle against the tundra. Aside from influences of climate and soil, the existence of the tundra-forest ecotone may owe its origin to the grazing of caribou and other wild life.

REFERENCES

BROOKS, A. A. 1953. Blazing Alaska's Trails. Univ. Alaska and Arctic Inst. of North America.

DACHNOWSKI-STOKES, A. P. 1941. Peat resources in Alaska. U.S.D.A. Tech. Bull. No. 769.

FILATOV, M. M. 1945. Geography of Soils of the U.S.S.R. Uchpedgiz, Moscow.

GLINKA, K. D. 1927. Outline of Soils of Yakutsk Region. In P. V. Wittenburg's Yakutia. Acad. Sci. U.S.S.R. Leningrad.

—— 1931. Soil Science. 4th ed. Moscow.

HUIKARI, O. 1952. On the determination of mire types, especially considering their drainage value for agriculture and forestry. Silva Fennica, **75**, 1–22.

KELLOGG, C. E., and NYGARD, I. J. 1951. Exploratory study of the principal soil groups of Alaska. U.S.D.A. Agric. Monogr. No. 7.

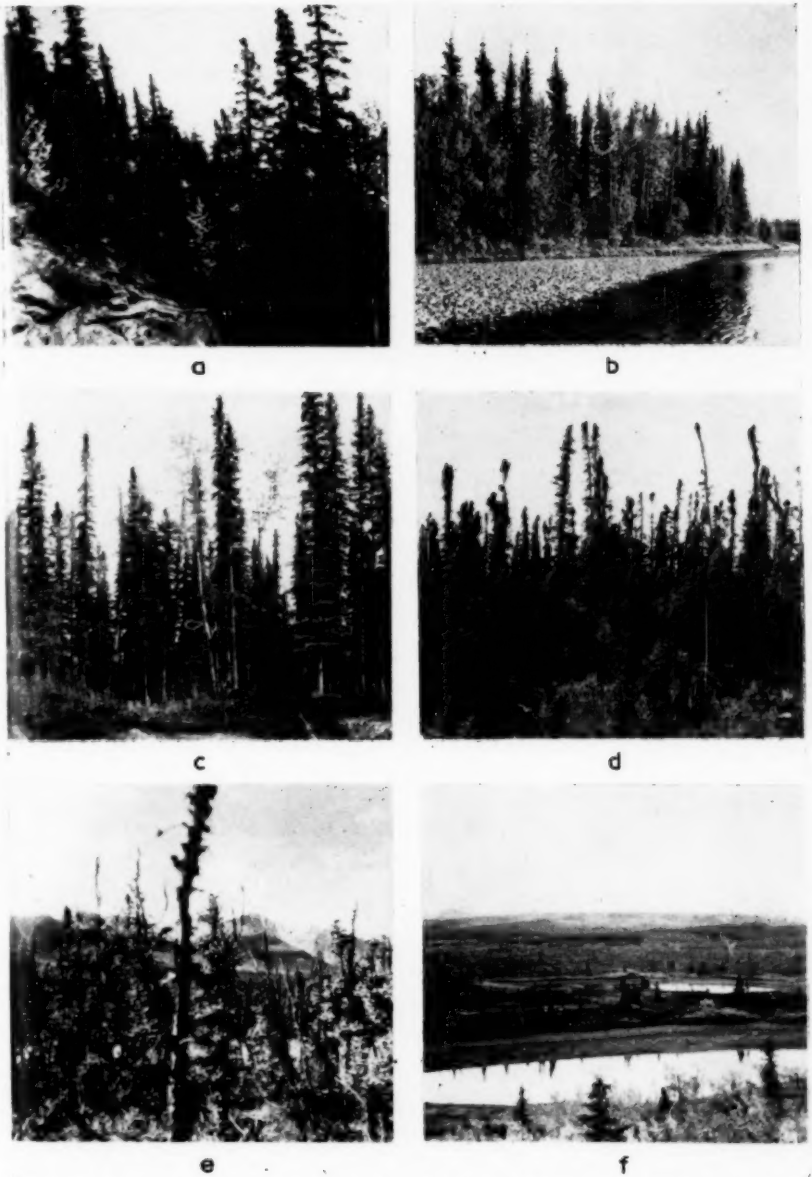

Plate I. Representative soil-forest units of interior Alaska: (*a*) white spruce on andesitic lithosol; (*b*) white spruce with some trembling aspen, paper birch, and tacamahaca poplars on an alluvial deposit; (*c*) white spruce on a weakly melanized raw-humus soil developed on micaceous loess; (*d*) white and black spruce on a gley podzolic loam underlain by permafrost at a depth of about 3 ft.; (*e*) black spruce on highmoor peat; (*f*) tundra-forest transition with sporadic occurrence of black spruce and clumps of Sitka alder, bog birch, and willows. (Photo (*b*) courtesy of the U.S. Air Force, Base Photo Lab., Ladd AFB, Alaska.)

S. A. WILDE AND H. H. KRAUSE—PLATE I

KRAUSE, H. H., RIEGER, S., and WILDE, S. A. 1959. Soils and forest growth on different aspects in the Tanana watershed of interior Alaska. Ecology, **40**, 492–5.
LUTZ, H. J. 1956. Ecological effects of forest fires in the interior of Alaska. U.S.D.A. Tech. Bull. No. 1133.
MIKHAILOV, N. I. 1956. Siberia, a Physico-Geographic Outline. Gosizdat, Moscow.
MOROZOV, G. F. 1930. Forest Types. Selkhozgiz, Moscow.
WILDE, S. A., VOIGT, G. K., and PIERCE, R. S. 1954. The relationship of soils and forest growth in the Algoma district of Ontario, Canada. J. Soil Sci. **5**, 1–17.
—— and KRAUSE, H. H. 1959. Alkali soils of Alaska. Report to the Director of the Alaska Experiment Station. Palmer, Alaska.
—— and VOIGT, G. K. 1959. Analysis of Soils and Plants. 2nd ed. Edwards, Ann Arbor, Mich.

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CUTANS: THEIR DEFINITION, RECOGNITION, AND INTERPRETATION

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Summary

The term cutans is proposed for a broad group of pedological features, including so-called 'clay skins', associated with the surfaces of the skeleton grains, peds, and various kinds of voids within soil materials. The chief differentiating characteristics of cutans are the kind of surface with which they are associated, the mineralogical nature of the cutanic material, and the fabric of the cutans themselves. Cutans can be interpreted on the basis of their characteristics in terms of the genetic processes of soil formation, and classified into simple and compound groups, each of which can be sub-divided into illuviation, diffusion, and stress types, composed of particular materials. The effects of cutans on profile development and plant growth may be considerable and their characteristics may dominate the characteristics of the soil material.

I. Introduction

EXPERIENCE has shown that one of the more obvious and common developments of soil structure[1] during profile development is the formation of concentrations and separations of fractions of the plasma associated with natural surfaces within the soil material. These natural surfaces are the faces of peds, skeleton grains, and the various kinds of voids, where the greatest reorganization of plasma is to be expected. This paper deals with a group of pedological features which are related to these natural surfaces within soil materials. Such features are important in the interpretation of soil genesis because they represent a striking segregation and reorganization of some of the constituents. Usually they occur in an orderly distribution down the profile and the method of translocation, segregation, and reorganization poses a fascinating problem. Such phenomena may be important in their effect on plant growth because of the segregation of soil constituents, modification of pore size and shape distributions, &c.

[1] Terms referring to structure and fabric used in this paper have been defined previously (Brewer and Sleeman, 1960), but are repeated here for completeness.

1. Soil structure is the physical constitution of a soil material as expressed by the size, shape, and arrangement of the solid particles—of primary particles to form compound particles and of the compound particles themselves—and voids.

2. Soil fabric is the physical constitution of a soil material as expressed by the spatial arrangement of the solid particles and associated voids.

3. The plasma of a soil material is that part which is capable of being, or has been, moved, reorganized, and/or concentrated by the processes of soil formation.

4. The skeleton grains of a soil material are individual grains which are relatively stable and not readily translocated, concentrated, or reorganized; it includes mineral grains and resistant siliceous and organic bodies larger than colloidal size.

5. Pedological features are recognizable units within a soil material which are distinguishable from the enclosing material for any reason such as origin, change in concentration of some fraction of the plasma, or change in arrangement of the constituents (fabric).

II. Nomenclature

In recent years the terms 'clay skins' and *Tonhäutchen* have been used to refer specifically to both 'skins' and 'clay'. They have a strong genetic inference indicating that the surfaces of peds or the walls of voids have been coated with 'clay' by deposition after illuviation in suspension. These phenomena are usually recognized (in reflected light with magnifications up to 60×) by their waxy lustre and/or irregular shape, 'like the appearance of tallow which has run down the side of a candle and hardened' (Kubiena, 1938). A closer study of phenomena identified as 'clay skins' has shown that there are many variations in the kind and arrangement of the material, which cannot be determined by reflected light characteristics. In particular, surface lustre is extremely sensitive to changes in organization of material so that a difference in lustre between the broken interior of a ped and the ped surface may be due to a change in organization (fabric) only.

It is considered, then, that the terms 'clay skins' and *Tonhäutchen* are inappropriate because:

1. In their normal usage they mean 'coatings of clay' and such an identification cannot always be made by the methods used. For example, the reflected light characteristics of slickensided surfaces, due to *in situ* modification of plasma, may be indistinguishable from those of a deposited clay film.
2. 'Clay' is a broad, not precisely defined term. Generally to soil workers it means any material whose particle size is less than 2μ equivalent diameter. However, to some workers it means particular mineral species irrespective of size.

For the study of soil genesis it is necessary to distinguish *in situ* surface modifications from depositions of illuviated plasma as well as deposition from suspension and deposition from solution. It is also necessary to recognize materials of various mineralogical and/or chemical composition.

Because of these considerations it is proposed to coin a new term, CUTAN[1] (plural form cutans; adjectival form cutanic), to include all the variations in the phenomena of coatings on the walls of voids, as well as *in situ* modifications of the plasma at such surfaces. Thus, a cutan is defined as a modification of the texture, structure, or fabric at natural surfaces in soil materials due to concentration of particular components or *in situ* modification of the plasma; cutans can be composed of any of the component substances of the plasma. By definition, cutans fall into the group of pedological features. Cutans which are the result of deposition or diffusion of plasmic material are plasma concentrations while those formed by *in situ* modification of the plasma are plasma separations.[2]

[1] The term cutan is derived from the Latin *cutis* meaning 'a coating, rind, or surface of a thing' (Gepp and Haigh, 1928); the ending has been changed for convenience in usage and so that the term can be defined without fear of confusion due to attempted translations of the original Latin.

[2] *Plasma concentrations* can be composed of any of the fractions of the plasma. *Plasma separations* are features characterized by a significant change only in the arrangement of the constituents (fabric) and not in concentration of constituents.

Although the definition is strongly genetic, cutans are recognized by their location (distribution pattern) as evidenced by a change in concentration, texture, structure, or fabric. The definition has been made very broad purposely so that the term can be used by field pedologists and cutans recognized in the field can be classified according to the data obtainable by field methods. For example, all the phenomena which have been identified as 'clay skins' are, in fact, cutans irrespective of the method of formation. However, identification of the varieties of cutans is properly a function of detailed laboratory study although it may be possible to qualify the broad identification of cutans by field observations.

A limited number of varieties of cutans are shown in Plates I and II. These will be referred to later as examples of particular characteristics of cutans.

III. Differentiating Characteristics

Cutans are recognized by their distribution with regard to natural surfaces within the soil material. They are sub-divided according to characteristics of the surfaces with which they are associated and the structure, texture, or fabric of the cutan itself. A further sub-division can be made on the basis of the kind of material of which they are composed. The most useful sequence for considering these criteria is:

1. The nature of the surfaces affected.
2. The kind of cutanic material.
3. The fabric of the cutans.
4. Additional features.

By using these data additional descriptive adjectives can be applied to the term cutan.

(*a*) *The characteristics of the surfaces affected*

For the study of soil genesis it is necessary to distinguish between cutans occurring on the various kinds of natural surfaces within soil materials, that is, on the walls of the various kinds of voids and the surfaces of skeleton grains, peds, other pedological features, &c. Experience so far suggests that the following separations should be made, with the probability that others will be necessary with broader experience.

1. *Grain cutans* are associated with the surfaces of skeleton grains or other discrete units such as nodules, concretions, &c. There are two types:

(*a*) *Free grain cutans* (Plate II, Photomicrograph 6) occur on the surface of skeleton grains which form the walls of the voids; such an arrangement results from the normal packing of skeleton grains in a loose sand. The loosely packed skeleton grains usually adhere to their neighbours at the points of contact because of the binding effect of the cutanic material.

(*b*) *Embedded grain cutans* (Plate II, Photomicrograph 4) occur on the surface of skeleton grains which are embedded in a relatively dense matrix of plasma. Displacement of the skeleton grains reveals cutanic material either adhering to the grains or on the surfaces of the impression

left by its removal. The cutans are not visibly (megascopically or microscopically) connected to voids which could act as conducting channels.

2. *Ped cutans* (Plate I, Photograph 1; Plate II, Photomicrograph 2) are associated with the surfaces of peds, that is, the walls of interpedal voids. They can be sub-divided into primary, secondary, tertiary, &c., according to the order[1] of the peds with which they are associated. They can also be sub-divided according to the shape of the interpedal voids.

3. *Channel cutans* (Plate I, Photograph 2; Plate II, Photomicrograph 5) are associated with the walls of acicular voids whether these be of biological origin (worn channels, &c.) or not.

4. *Plane cutans* are associated with the walls of planar voids other than those which occur between peds. There are three types which are not always easily distinguishable:

(*a*) *Joint-plane cutans* (Plate I, Photograph 3) are associated with the relatively flat, smooth surfaces of planar voids which traverse the soil material in some fairly regular pattern. Usually several such voids form a parallel pattern or system of planes. There may be more than one of these systems in a soil material.

(*b*) *Slip-plane cutans* are associated with the surfaces of planar voids which also show evidence of differential movement. Slip-planes are recognized by the occurrence of striations and/or elongated crests and depressions on the plane surfaces.

(*c*) *Contraction-plane cutans* (Plate II, Photomicrograph 3) are associated with the surfaces of planar voids which result from soil contraction on drying. Contraction planes are recognized by their irregular distribution pattern and irregular surfaces.

5. *Normal void cutans* are associated with the walls of the normal voids which occur within primary peds or in unaggregated soil materials.

(*b*) *The mineralogical nature of the cutanic material*

Identification of the cutanic material is done optically and by analysis after isolation by dissection. At the present state of knowledge the following separations should be attempted; others, no doubt, will be necessary as experience grows. Crystallinity, size, and shape of the plasma grains may be useful as characteristics for further sub-division.

1. *Clay minerals.* The term 'clay minerals' is used advisedly in contrast to the general term 'clay'. It refers dominantly to the layer lattice minerals, the attapulgites, sepiolites, and palygorskites, the chlorites and the allophane types; crystalline oxides, carbonates, and sulphides are excluded from the clay mineral group for the purpose of classifying cutans. In reflected light, thin clay mineral cutans have a smooth, glazed surface while thick ones have an uneven, ropy appearance with waxy lustre. They are sub-divided according to the contaminants on the basis of colour and reaction to a few simple spot tests. A more detailed subdivision is possible on the basis of identification of the kind of clay

[1] Primary peds are the smallest recognizable peds and they may be packed so as to form larger complex secondary peds which in turn may be arranged to form tertiary peds, and so on.

mineral and measurement of the size and shape of the individual clay mineral grains.

(*a*) *Pure clay minerals*. The material is white, creamy, or pale grey. Such cutans are rare but do occur (Beattie and Haldane, 1958).

(*b*) *Clay minerals with iron oxides or hydroxides* (Plate II, Photomicrographs 1, 6). The material is coloured in shades of yellow, red, green, or blue. Ignition produces a bright red colour and comparison of this with the original colour gives some idea of the degree of hydration or oxidation. Clay mineral cutans may vary in degree of hydration and oxidation of the iron compounds within a single cutan.

(*c*) *Clay minerals with organic matter* (Plate I, Photographs 1, 2; Plate II, Photomicrograph 2). The material is grey to dark grey. The degree of charring on heating gives some indication of the amount of organic matter and ignition reveals the presence or absence of iron compounds.

2. *Sesquioxides*. The material may have a glazed appearance but no waxy lustre in reflected light. If iron oxides or hydroxides are present it is red, yellow, blue, or green in reflected light according to the degree of hydration and oxidation; ignition produces the typical bright red colour of ferric oxide and solution by Jeffries' method (Jeffries, 1946) or the dithionite method (Aguilera and Jackson, 1953) leaves little or no residue. In thin section cutans of iron oxides or hydroxides are translucent to opaque and usually isotropic. Aluminium oxides and hydroxides are difficult to identify in cutans since they are usually associated with the highly coloured iron minerals. Probably the best method is X-ray analysis of dissected cutanic material.

3. *Manganese oxides or hydroxides* (Plate I, Photograph 3; Plate II, Photomicrograph 3). The material may have a glazed appearance and is very dark brown to black in reflected light; it is usually opaque in thin section. The periodate method (Piper, 1942) will identify the presence of manganese quantitatively.

4. *Soluble salts* (*carbonates, sulphates, chlorides, &c.*) (Plate II, Photomicrograph 5). The material occurs as a fine white powdery efflorescence or as masses of coarser crystals. It is usually white or colourless with yellow and grey tints; it may have a glassy or dull earthy lustre according to the degree of crystallization. The various salts can be identified by separation, solution and micro-tests and flame tests; coarser crystals can be identified optically.

5. *Silica*. It is possible to have cutans of silt- or clay-size quartz. Genetically it is important to distinguish primary from secondary quartz but in practice this is difficult. Staining tests for amorphous silica have been used (Kubiena, 1938) but are generally unsatisfactory. Infra-red absorption (Fieldes *et al.*, 1956) has also been used.

(*c*) *The fabric of the cutans*

Further sub-divisions of cutans can be made on the basis of the physical arrangement (fabric) of the cutanic material. These characteristics can be described under the following headings in the terms set out by Brewer and Sleeman (1960).

1. *Sharpness of boundary*. From very diffuse to sharp.
2. *Orientation pattern*.

(*a*) *Orientation of the plasma grains with each other* (Plate II, Photomicrographs 1, 2, 4, 5, 6). At various magnifications the plasma grains may appear strongly oriented, moderately oriented, weakly oriented, unoriented, indeterminate (due to size or kind of material), or crystallized (as recognizable crystals). In addition the orientation may be continuous (the cutan is a single strongly oriented unit), striated (elongated strongly oriented plasma aggregates arranged parallel to each other), or flecked (plasma aggregates arranged randomly).

(*b*) *Orientation of the plasma grains with regard to the cutanic surfaces* (Plate II, Photomicrographs 1, 2, 4, 5, 6). Parallel, normal, transverse, or unrelated orientation with regard to the cutanic surfaces.

(*d*) *Additional characteristics*

For the interpretation of soil genesis, as opposed to identification and structure descriptions, two other characteristics may be important and should be described.

1. *Degree of separation*. The degree of separation deals with the degree of contrast in fabric or concentration of material between the cutanic and the non-cutanic soil material. It is recorded as *slightly separated* where there is just an observable difference, through *weakly separated* (where there is a definite difference) and *moderately separated* (where there is a great difference) to *strongly separated* where the characteristics of the cutanic material are entirely those due to the characteristics of the concentrated component of the plasma or where there is a great decrease in the proportion of skeleton grains in the cutanic material. All the cutans shown in Plates I and II are strongly separated.

2. *Degree of adhesion*. The degree of adhesion refers to the strength of adhesion between the cutanic material and the cutanic surfaces. It is estimated by the amount of cutanic material adhering to the cutanic surfaces after gentle crushing. It is recorded as *free* when virtually none of the surfaces are coated with cutanic material after gentle crushing, through *weakly adhesive* (less than 30 per cent. of the surfaces coated after crushing) and *moderately adhesive* (30 to 60 per cent. coated) to *strongly adhesive* when more than 60 per cent. of the surfaces are coated after gentle crushing.

IV. Classification and Interpretation

Although insufficient data is available as yet to be precise about the genetic interpretation of all the various kinds of cutans, the task can be made somewhat simpler by attempting to classify them into broad groups.

(*a*) *Classification*

Cutans can be classified into two main groups:

1. *Simple cutans* are composed of a single mineralogical and/or chemical substance or of a uniformly intimate mixture; there is no layering effect in composition or fabric and the cutan has been formed

by a single process. All the cutans shown in Plates I and II are simple types except Plate II, Photomicrograph 5.

2. *Compound cutans* (Plate II, Photomicrograph 5) are composed of alternate layers of mineralogically and/or chemically different substances, or of different fabrics; more than one process may be involved in their formation.

These two broad groups can be sub-divided on the basis of process of formation into:

(i) *Illuviation cutans* (Plate II, Photomicrographs 1, 2, 5, 6), which are true coatings due to movement in solution or suspension and subsequent deposition.

(ii) *Diffusion cutans* (Plate II, Photomicrograph 3), which are concentrations at the surface due to diffusion; they may be coatings or concentrations within the soil material which reach a maximum at the cutanic surface.

(iii) *Stress cutans* (Plate II, Photomicrograph 4) are *in situ* modifications of the plasma due to differential forces such as shearing; they are not true coatings. Most stress cutans are simple types.

(iv) *Complex cutans* are those formed by a combination of more than one of the above processes.

Divisions at lower levels can then be made on the morphological characteristics of cutans set out earlier.

With the present state of knowledge it is not always possible to classify any particular observed cutan completely. It is suggested, therefore, that qualifying adjectives should be applied to the term cutan just so far as evidence will allow. The operative adjectives in their order of importance are:

1. Kind of surface affected.
2. Simple or compound cutan.
3. Illuviation, diffusion, stress, or complex cutan.
4. Kind of cutanic material.
5. Orientation pattern.
6. Sharpness of boundary.
7. Degree of separation.
8. Degree of adhesion.

These can be used individually or collectively according to the evidence available. If 1, 2, and 3 are used they should precede the noun; the other terms are best used after the noun, thus: 'Simple, illuviation, joint-plane cutan composed of clay minerals with strong, continuous, parallel orientation, sharp boundary, strong separation and weak adhesion.' Such a statement provides the interpretation and the observed evidence for such an interpretation.

(*b*) *Interpretation*

If the cutans present in a soil material can be classified as simple or compound and further into one of the four groups at the next level, a great amount of information concerning the processes of formation of

the soil material has been achieved. This can be amplified by identification of the cutanic material and measurement and comparison of its amount with non-cutanic material. The greatest need, then, is for a list of characteristics for classifying cutans at the two highest levels. This is the interpretative stage of the study and at the present state of knowledge such interpretations must necessarily be largely tentative. More definite and dependable interpretations will be possible as experience grows, particularly if the various kinds of cutans can be reproduced under controlled conditions in the laboratory.

At present certain facts are known and some other inferences seem legitimate.

1. Usually there is little difficulty in classifying cutans as simple or compound on evidence from thin sections (Plate II). Simple cutans indicate relatively uniform conditions during their formation, whereas compound cutans indicate the operation of one or more changes in conditions. Two relatively common forms of compound cutans are:

(i) Several alternate layers of clay minerals and iron oxides, which indicate alternating conditions suitable for separation of these components.

(ii) A layer of clay minerals between a layer of calcite and the cutanic surface (Plate II, Photomicrograph 5) indicating a drastic change in conditions. Normally the layer of material closer to the cutanic surface is separated before that farther away but in many calcite-clay mineral cutans the calcite forms a cohesive tube before the clay mineral material is deposited between it and the cutanic surface.

2. The real difficulty in interpretation of cutans is to distinguish between illuviation, diffusion, and stress cutans. However, an examination of their characteristics gives some logical basis for interpretation. The distinguishing features are set out in Table I.

(i) *Kind of cutanic material.* The cutanic materials can be divided into:

(*a*) Those which form suspensions and readily undergo reorientation, such as the clay minerals.

(*b*) Those which form solutions or suspensions but are not readily reoriented, such as the oxides and hydroxides of iron, secondary silica, &c.

(*c*) Those which form solutions, such as hydroxides, oxides, and soluble salts.

The first group can form deposition or stress cutans but are unlikely to form diffusion cutans while the second and third groups can form deposition or diffusion cutans but are unlikely to form stress cutans.

(ii) *Fabric of the cutanic material.*

(*a*) *Sharpness of boundary.* In general, the sharper the boundary between the cutanic material and non-cutanic material the more definite is the diagnosis as an illuviation cutan. Similarly, the more diffuse the boundary the more definite is the diagnosis as a diffusion or stress cutan. However, it is possible for all of these types of cutan to have sharp or diffuse boundaries at the magnifications possible with a petrological microscope.

(*b*) *Orientation pattern.* Typically, strong orientation of the plasma

TABLE I

Diagnostic Characteristics of Cutans

Characteristic	*Kind of cutan*			
	Illuviation		*Diffusion*	*Stress*
1. Kind of material	(*a*) Those which form suspensions and readily undergo reorientation	(*b*) Those which form solutions or are not readily reoriented	Those which form solutions	Those which readily undergo reorientation
2. Sharpness of separation	Sharp	Sharp	Diffuse (to sharp)*	Diffuse (to sharp)
3. Orientation pattern	Strong continuous (to weak, flecked)	Crystallized to indeterminate	Crystallized to indeterminate	Moderate, striated (to strong, continuous) with associated striated sub-cutanic plasma
4. Distribution pattern	Associated with conducting voids	Associated with conducting voids	Associated with voids of any size or shape	Associated with planar voids or embedded skeleton grain surfaces
5. Degree of separation	Strongly separated	Strongly separated	Strongly separated	Weakly to moderately separated and associated with weakly separated to unseparated subcutanic material with striated orientation

* The characteristics in brackets may occur but are less useful diagnostically than those not in brackets.

grains with regard to each other is indicative of illuviation clay mineral cutans; simple, illuviation, free grain cutans composed of clay minerals have been produced in the laboratory and always had strong, continuous orientation (Brewer and Haldane, 1957). In certain circumstances, however, illuviation clay mineral cutans have moderate or weak, striated or flecked orientation (Plate II, Photomicrograph 2) and illuviation cutans of other materials are unoriented, indeterminate or crystallized (Plate II, Photomicrograph 5). Stress cutans are often very thin and the orientation in the cutanic material difficult to see, but typically they have associated with them a striated orientation of the sub-cutanic plasma (Plate II, Photomicrograph 4). Diffusion cutans typically are crystallized or have an indeterminate orientation (Plate II, Photomicrograph 3).

(*c*) *Distribution pattern.* Illuviation cutans are always associated with conducting voids. Nothing is known at present concerning the size of the void through which particles of particular size and shape will pass in suspension, but experience suggests that illuviation clay mineral cutans are usually associated with voids which can be seen under the microscope at magnifications up to 800×. Illuviation cutans of soluble materials may be associated with much smaller voids. Diffusion cutans can be associated with voids of any size. Stress cutans are associated with planar voids or surfaces of skeleton grains embedded in a dense matrix, that is, there may be no visible voids.

(iii) *Degree of separation.* Typically, illuviation cutans are strongly separated since they consist entirely of the deposited material and so contrast strongly with the undifferentiated materials of the soil mass. Similarly, diffusion cutans are often strongly separated. Stress cutans may have any of the degrees of separation; usually they are weakly to moderately separated and the associated sub-cutanic material with striated orientation is weakly separated to unseparated.

V. Discussion

The occurrence of cutans in soil materials is of considerable importance in several aspects of soil studies. The effect of their presence on the course of soil formation, on the properties of the soil materials in regard to plant growth, and the interpretation of analytical data must be very considerable. This is so even when cutans are quite thin and comprise only a relatively small proportion of the soil material by volume or by weight, since their effect can be considerable because of their large surface area per unit volume. In addition, there is considerable evidence that, in general, cutan formation becomes progressively more dominant as soil profiles become older (Walker, 1959; Churchward, 1959) so that its effect may be cumulative.

As cutans develop in a soil material and form an increasing proportion of it they tend to isolate portions by means of a protective film of materials of various kinds. Since the cutans occur on natural surfaces in the soil materials such as walls of voids, surfaces of peds and grains, they will tend to protect the bulk of the soil material from many processes, especially leaching, and may drastically change the course of soil

formation. In addition, the nature of the soil material will change in so far as a material without cutans will behave as a porous medium allowing movement and reorganization of the soil constituents according to the laws of movement in such a medium. However, with the development of cutans the characteristics of the material change radically and many of its properties will approximate those of a colloid membrane composed of various materials adhering to a relatively inert matrix. It is probable, too, that the course and rate of mineral weathering in a porous medium will be quite different from those in a medium which is protected by cutans. The laboratory study of processes operating in these two different media obviously will require quite different models and approaches.

The occurrence of cutans will also have a considerable effect on plant growth, not only because of their effect on the course of soil formation but more immediately because they affect the environment of the plant roots. In the soil material shown in Plate I, Photographs 1 and 2, the plant roots are confined to the ped faces and channels both of which are coated with thick illuviation cutans composed of clay minerals contaminated with organic matter. The bulk of the soil material has quite a high proportion of coarse and fine sand but the environment of the plant roots is dominated by the characteristics of the very fine-grained clay mineral cutans. Similarly the soil material shown in Plate I, Photograph 3, imposes an environment dominated by the characteristics of highly manganiferous cutans on many of the pla[illegible]ots. In both these examples much of the soil material is isolated fro[illegible]e activity of the plant roots so that plant growth must be affected. Rovira and Greacen (1957) have shown that plant nutrients can be unavailable to plants because of a physical locking away. Undoubtedly the presence of cutans will amplify this effect.

These effects of cutans lead to a consideration of the most useful kinds of soil analyses and the interpretation of the usual routine analyses in terms of soil formation and plant growth. It is apparent that for a soil without cutans whose characteristics approximate those of a porous medium the usual analyses of the whole soil material are useful criteria for soil formation and plant growth. However, in soil materials which have strongly developed cutans, the important analytical data is that of the cutanic material and not of the whole soil material. In such materials interpretation of analyses of the whole soil material is impossible or misleading in regard to the course of profile development or plant growth. Such soil materials can be properly characterized only by two separate sets of data, one for the bulk of the material and one for the cutanic material.

The effects of cutans will depend on their degree of development, the nature of the cutanic material, their distribution in the particular soil material and their distribution in the soil profile. Usually their degree of development, and perhaps the nature of the cutanic material, varies within a soil profile so that cutans composed of different materials may reach a maximum of development in different horizons in the one soil profile.

VI. Acknowledgements

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REFERENCES

AGUILERA, N. H., JACKSON, M. L. 1953. Iron oxide extraction from soils and clays. Soil Sci. Soc. Amer. Proc. **17**, 359.

BEATTIE, J. A., HALDANE, A. D. 1958. The occurrence of palygorskite and barytes in certain parna soils of the Murrumbidgee region, New South Wales. Aust. J. Sci. **20**, 274.

BREWER, R., HALDANE, A. D. 1957. Preliminary experiments in the development of clay orientation in soils. Soil Sci. **84**, 301.

—— SLEEMAN, J. R. (1960). Soil structure and fabric: their definition and description. J. Soil Sci. **11**, 172.

CHURCHWARD, H. M. 1959. Pedological significance of groundsurface development in an aeolian landscape: a study of the soils near Swan Hill. M.Sc. Thesis, Univ. of Sydney.

FIELDES, M., WALKER, I. K., WILLIAMS, P. P. 1956. Clay mineralogy of New Zealand soils R-3. Infra-red absorption spectra on soil clays. N.Z. Jour. Sci. Tech. **38**, 31.

GEPP, C. G., HAIGH, A. E. 1928. Latin–English Dictionary. Longmans, Green and Co., London.

JEFFRIES, C. D. 1946. A rapid method for the removal of free iron oxides in soil prior to petrographic analysis. Soil Sci. Soc. Amer. Proc. **11**, 211.

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PIPER, C. S. 1942. Soil and Plant Analysis. Hassell Press. Adelaide.

ROVIRA, A. D., GREACEN, E. L. 1957. The effect of aggregate disruption on the activity of microorganisms in the soil. Aust. Jour. Agric. Res. **8**, 659–73.

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PLATE I. *Megascopic Characteristics of Some Cutans*

Photograph 1. The dark material on the left of the fractured prismatic ped is a simple, illuviation, ped cutan composed of clay minerals with organic matter, with a sharp boundary and moderate adhesion.

Photograph 2. The dark material ramifying the fractured ped is a series of simple, illuviation channel cutans composed of clay minerals with organic matter, with a sharp boundary and moderate adhesion.

Photograph 3. The dark material running across the soil block occurs on the surface of the plane and constitutes simple, illuviation, joint-plane cutans composed of manganese oxides, with a sharp boundary and strong adhesion.

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Micrograph 1. (×9) The very strongly oriented clay material constitutes a simple illuviation, channel cutan composed of clay minerals with iron oxides, with strong, continuous, parallel orientation and sharp boundary.

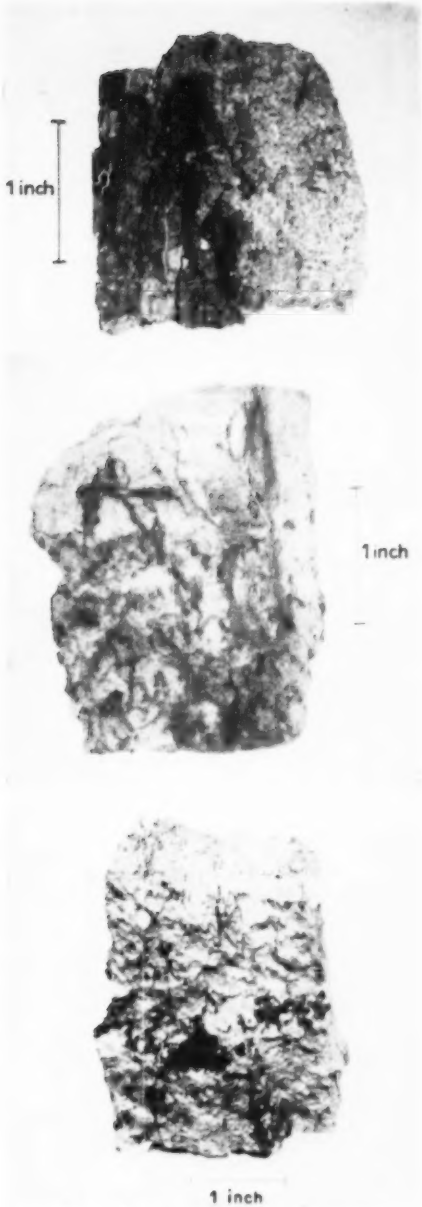
Micrograph 2. (×8) The flecked clay material constitutes a simple illuviation, ped cutan composed of clay minerals with organic matter, with strong, flecked, unrelated orientation and sharp boundary. This is the same material shown in Plate I, Photograph 1.

Micrograph 3. (×11) The black material associated with fine cracks constitutes simple, diffusion (?), contraction-plane cutans composed of manganese oxide, with diffuse boundary.

Micrograph 4. (×11) The clay material with striated parallel orientation surrounding some of the quartz grains indicates the presence of simple, stress, embedded grain cutans.

Micrograph 5. (×9) Compound, illuviation, channel cutan composed of clay minerals and calcite. The clay minerals have very strong, continuous, parallel orientation and sharp boundary. The calcite is crystallized and unoriented.

Micrograph 6. (×13) Simple, illuviation, free grain cutans composed of clay minerals with ferric hydroxides, very strong, continuous, parallel orientation and sharp boundary.



Illustrating some varieties of cutans.

R. BREWER—PLATE I

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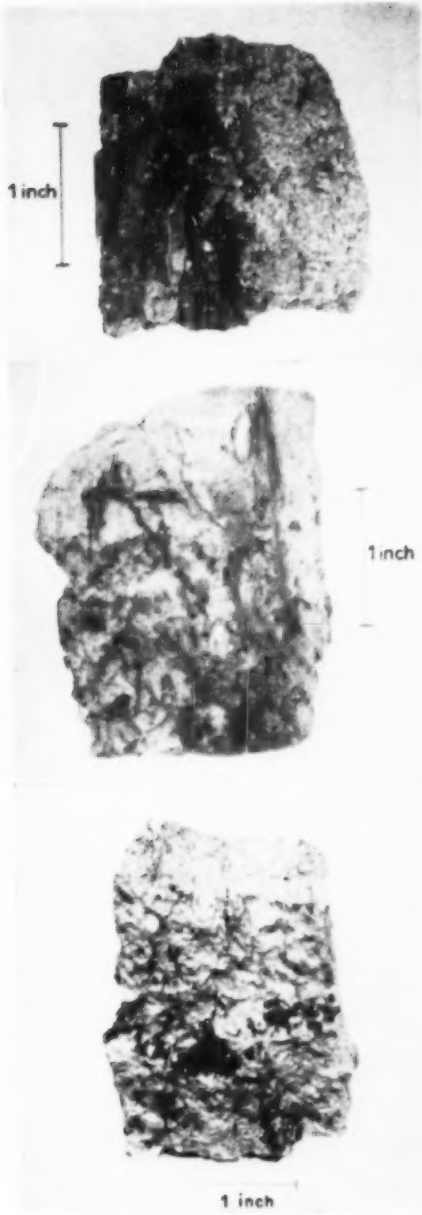

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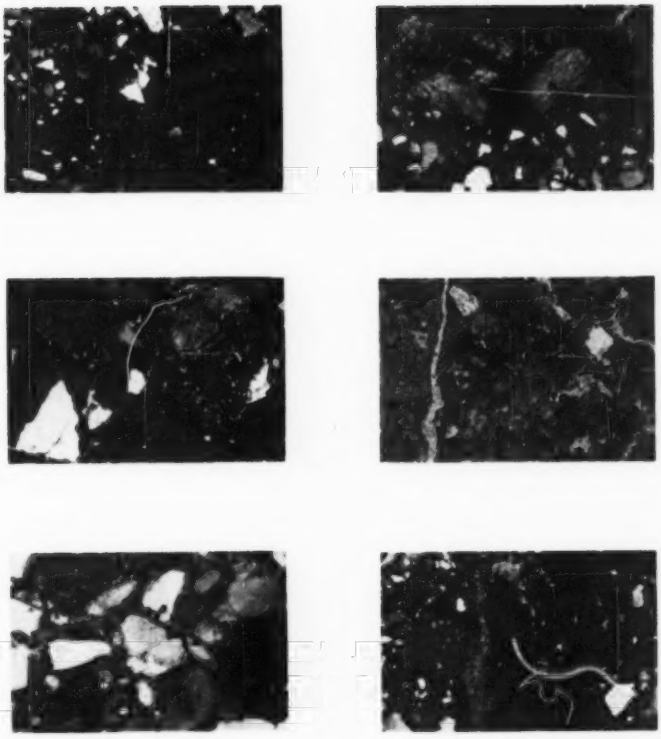

Illustrating some varieties of cutans.

R. BREWER—PLATE II

A TREATMENT OF THE CAPILLARY FRINGE IN THE THEORY OF DRAINAGE

II. MODIFICATIONS DUE TO AN IMPERMEABLE SUB-STRATUM

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(*University of Cambridge School of Agriculture and Agricultural Research Council Unit of Soil Physics*)

Summary

When a drainage system copes with both artesian and precipitated water the streamline dividing the two flow zones passes through a stagnation point in the medial vertical plane parallel to the drain lines. The approximation is made that the water-table and capillary fringe boundary may be regarded as those appropriate to precipitated water only, in the presence of an impermeable bed passing through the stagnation point. While the absolute heights may be in error it is shown that the partition of the capillary fringe about the water-table location in the absence of a fringe is given with only small error. This partition is calculated from hodograph theory with the aid of Edsac II for combinations of three values of precipitation rate, seven values of fringe thickness, and nine values of depth of impermeable bed. By interpolation, curves are presented to show the partition for combinations of three selected precipitation rates, five depths of bed, and continuous variation of fringe thickness. It is shown that for high precipitation rates the greatest fringe thicknesses are accommodated almost wholly above that surface which would have been the water table in the absence of a fringe, while for the lowest rates of precipitation and zero bed depth only 30 per cent. of the fringe is so accommodated; the remainder is below.

In an earlier paper, which will be referred to as Part I (Childs, 1959), it was shown that the hodograph method of analysis of the land-drainage problem (van Deemter, 1950) is capable of a slight modification which enables one to compute by this means both the water-table height and the configuration of the boundary of the capillary fringe. That analysis is unfortunately applicable only where there is infinitely deep material of uniform hydraulic conductivity. Further consideration shows, however, that when there is an impermeable substratum at such a depth that its presence may not be ignored it is possible to introduce an approximation which may be expected to elucidate the modifications due to such a layer, although it is not to be expected that this approximation should treat validly the absolute heights of the surfaces referred to.

The Nature of the Approximation

The most general case of flow within the boundaries defining the problem is shown in Fig. 1, which includes a few key streamlines. Here we have, using the same notation as in Part I, a flux N (positive upward) across the fringe boundary and a flux L upward at great depth representing artesian flow. When N represents a net downward flow, as when precipitation exceeds evaporation, it takes a negative value, say $-q$; the flow net is drawn for this case in Fig. 1 since it is this case

with which we shall be concerned. The analysis given in Part I is of course quite general and applies whatever the sign of N and L.

Along the boundary RS the descending limiting streamline RO meets an opposing rising streamline SO, the two continuing to the drain P as the common streamline OP. The point O, where the streamlines suddenly change direction by $\pi/2$ and where the flow velocity is

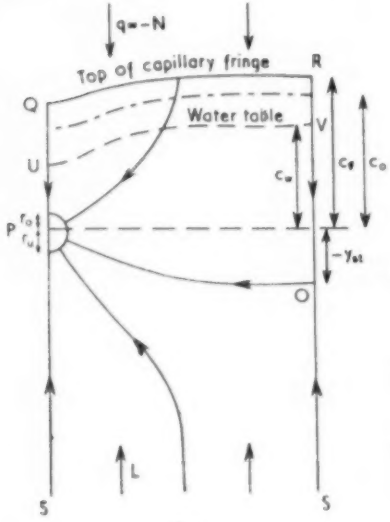

FIG. 1

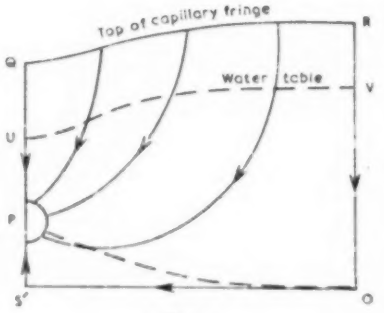

FIG. 2

FIG. 1. The boundaries of the problem, showing some key streamlines including the dividing streamline OP. — — — — — — — — Water-table position when there is no capillary fringe.

FIG. 2. The boundaries of the problem of drainage of precipitated water in the presence of an impermeable substratum, which passes through the stagnation point O of Fig. 1. The broken line OP is the superimposed dividing streamline of Fig. 1.

consequently zero, is referred to as a stagnation point. The greater the ratio L/q the higher are the stagnation point and the dividing streamline OP.

A cut may be made along a streamline without affecting the flow net since on such a path there is no transverse flow. One may therefore divide the problem shown in Fig. 1 into two by cutting along OP; the upper part would then correspond to drainage of precipitated water only, with an impermeable substratum whose upper surface is represented by OP. We may compare in Fig. 2 the upper section thus obtained with a case of drainage of precipitated water in the presence of a flat horizontal impermeable bed passing through O; the cut bed is indicated by the broken line through O. The difference between the two is that a part of the flow zone which is available in the case of the flat bed is not available in that of the cut bed. The corner S' in Fig. 2

is also a stagnation point since here also the streamline suddenly changes direction by $\pi/2$; hence the flow in its neighbourhood is not large. The non-availability of this corner in the cut bed case might therefore be expected to have only minor consequences. It must be remembered, however, that not all the drain perimeter is used in the latter case. It might be expected that the height of the water table over the cut bed would be greater, but not much greater, than that of the water table over the flat bed. The only way as yet of examining the error involved is to compare a few cases calculated by hodograph theory with the results of electric analogue or relaxation studies of the corresponding flat bed cases. This has been done, with the collaboration of a colleague, in the absence of a capillary fringe and the results will be presented in due course; it is sufficient to indicate here that the water-table height calculated by hodograph analysis of the cut bed approximation is unlikely to exceed the water-table height above the horizontal flat bed at the depth O by more than 50 per cent.

An error of the magnitude indicated above for the absolute height of the water table would no doubt be considered unacceptable. The point to be made here is that the error would be about the same both for the calculation of the water-table height in the absence of a capillary fringe and for the calculation of the water-table and fringe-boundary heights with a specified capillary fringe. If c_f is the height of the fringe boundary in a specified case and c_0 is the height of this boundary (which also coincides with the water table) when the fringe thickness is zero, then both c_f and c_0 are subject to approximately the same error due to substituting the cut bed for the flat horizontal bed and the difference $c_f - c_0$ is subject to only small error, as also is the difference $c_w - c_0$ where c_w is the water-table height with a specified capillary fringe. Hence if we express our results, as in Part I, in the form of curves showing how the capillary fringe is partitioned above and below the position that the water table would have occupied had there been no capillary fringe, the error due to the approximation will be of second order only. The point will be referred to again in the discussion in the light of the results to be presented.

Method of Procedure

Equations (4) to (10) inclusive of Part I are derived from the general equations (51) and (52) of that paper for the special case where L has the value zero. The appropriate equations for finite L are listed below.

$$\gamma = (K-q)/(L+q) \tag{1}$$

$$(1+\beta) = [(1+\gamma)\tan\theta + \{1+(1+\gamma)^2\tan^2\theta\}^{\frac{1}{2}}]/[\tan\theta + (1+\tan^2\theta)^{\frac{1}{2}}] \tag{2}$$

$$\nu/\lambda = t_{sl} = [(K/q)\tan\theta + \{(K/q)^2\tan^2\theta + 1\}^{\frac{1}{2}}]/[\tan\theta + (1+\tan^2\theta)^{\frac{1}{2}}] \tag{3}$$

$$\pi c_f/a = \ln(1+2/\beta) + (2/\gamma)\ln(1+\beta/2) \tag{4}$$

Along the boundary RS we have

$$\pi y/a = \pi c_f/a + \ln \frac{\delta_a}{\delta_a + 2(1+\beta)} + (2/\gamma) \ln \frac{\delta_a + 2 + \beta}{\delta_a + 2(1+\beta)} \tag{5}$$

$$\pi h/a = (1 + L/K) \ln \frac{\delta_a + 2(1+\beta)}{\delta_a} + (L/K + q/K) \ln \frac{\beta + \delta_a}{2 + \beta + \delta_a} - \pi s/a \tag{6}$$

$$0 < \delta_a < \infty$$

$$\pi y_{st}/a = \pi c_f/a + (2/\gamma) \ln \frac{1+t}{1+\beta+t} + \ln \frac{t-1-\beta}{1+\beta+t} \tag{7}$$

where t has the value t_{st} as in (3) above, and is the same as ν/λ in equation (5a) of Part I.

Along PQ we have

$$\pi y/a = \pi c_f/a + \ln \frac{\beta + \delta_b}{2 + \beta - \delta_b} + (2/\gamma) \ln \frac{2 - \delta_b}{2 + \beta - \delta_b} \tag{8}$$

$$\pi h/a = (1 + L/K) \ln \frac{2 + \beta - \delta_b}{\beta + \delta_b} + (L/K + q/K) \ln \frac{\delta_b}{2 - \delta_b} - \pi s/a \tag{9}$$

$$0 < \delta_b < 1$$

Along PS we have

$$\pi y/a = \pi c_f/a + (2/\gamma) \ln \frac{2 + \delta_u}{2 + \beta + \delta_u} + \ln \frac{\beta - \delta_u}{2 + \beta + \delta_u} \tag{10}$$

$$\pi \phi/a = \pi c_f/a + (1/\gamma)(1 + q/K) \ln \frac{2 + \delta_u}{2 + \beta + \delta_u} + (q/K) \ln \frac{\delta_u}{2 + \beta + \delta_u} + \\ + (L/K) \ln \frac{\delta_u}{\beta - \delta_u} - \pi s/a \tag{11}$$

$$0 < \delta_u < \beta$$

Equation (3) is the same as (5 a) on p. 96 of Part I and equation (7) has no counterpart in Part I. With those exceptions equations (1) to (9) inclusive correspond respectively to (4) to (10) of Part I; the latter can be derived from the former by giving L the value zero.

The symbols are all in conformity with Part I; that is to say θ is the angle of steepest slope of the capillary fringe boundary and is an arbitrarily selected parameter for the purposes of our calculations; c_f is defined in Fig. 1; h is the hydrostatic pressure in centimetres of water and y is the vertical distance above the origin P at a point defined on the appropriate boundary by an arbitrary selection of the parameters δ within the stated limits. ϕ is the hydraulic potential at such a point, and s is the suction (manometric units) at the upper boundary of the capillary fringe, i.e. the suction at which the soil hydraulic conductivity becomes seriously impaired (see Part I, p. 84).

The procedure adopted is as described in Part I. Using equation (9) we vary θ and therefore β and δ_b systematically and find by trial and error that pair of values which gives one point and one only on PQ at zero pressure. This defines the 'optimum' drain equipotential, the

top of which has the ordinate r_0 given by y in (8) with the same pair of values of β and δ_b. This same value of β gives us c_f from (4). To find the water-table height c_w we choose a value of δ_a by trial and error which gives a zero value for h in (6), and this value of δ_a gives a value of y from (5) which supplies the value c_w. The revealed value of θ enables us to calculate t_{st} from (3) and this in turn gives us the ordinate of the stagnation point y_{st} in (7). This process is repeated for all combinations of selected values of q/K, L/q, and s/a.

The results obtained in Part I were calculated with the aid of a modern electric desk calculating machine, and the experience made it evident that repetition to cover the combinations referred to would constitute a very formidable task. Fortunately the electronic digital computer of the Cambridge University Mathematical Laboratory (Edsac II) was made available and the problem was programmed for this machine. Since volume of computation was then no obstacle the range of s variation was extended beyond that of Part I, the accuracy was much increased by refining the determination of the critical θ and δ values, and the ordinate of the drain invert was in each case calculated instead of being assumed to be given by $-r_0$. For this purpose equations (10) and (11) were used. By trial and error a value of δ_u was found which gave a potential ϕ, from (11), corresponding to that of the drain equipotential defined in the first stage of the calculation; i.e. δ_u was chosen to give ϕ the value r_0 which was already known. Substitution of this δ_u in (10) gave y, the ordinate of the drain invert, i.e. r_u.

The whole of the machine time, including programme testing, amounted to a few minutes short of 2 hours.

Presentation of Results

In the special case where s has the value zero the capillary fringe is of zero thickness; c_f and c_w coincide at the value c_0. In any other case of s (other factors remaining constant) c_f exceeds c_0 and c_w is less than c_0, i.e. the capillary fringe of total thickness $c_f - c_w$ is partitioned about c_0. The ratios $(c_f - c_0)/s$ and $(c_w - c_0)/s$ are convenient dimensionless quantities to express this partitioning, and as in Part I the results are presented in the form of curves in which these ratios are plotted as functions of $(\pi s/a)/(q/K)$. The fringe parameter s is expressed in this form because the range of s/a appropriately taken is proportional to q/K (see Part I, p. 92). Three separate sets of curves, Figs. 3, 4, and 5, are provided, one for each of the chosen values of q/K (namely 0·1, 0·01, and 0·001). Each set of five curves includes one for each of the chosen values of y_{st}/a (namely $-\infty$, $-0{\cdot}5$, $-0{\cdot}2$, $-0{\cdot}1$, and 0). The curves of Part I reappear here as the special case where y_{st} has the value $-\infty$. Figs. 6, 7, and 8 similarly show the ratios of diameter of optimum drain to that of the optimum drain in the absence of a capillary fringe, i.e. the ratios $(r_0 + r_u)/({}_0r_0 + {}_0r_u)$ where ${}_0r_0$ and ${}_0r_u$ are the values of r_0 and r_u for zero s. It must be remembered that, except for the case of zero L (i.e. infinite y_{st}), drainage from precipitated water flows to only a sector of the drain perimeter. Where these latter curves differ from those for zero L in Part I the reason is in part because the earlier paper

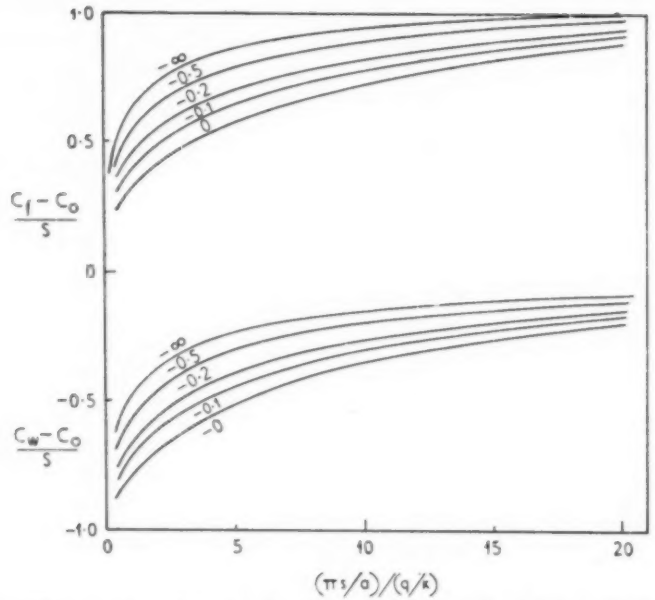

FIG. 3. The partition of the capillary fringe above and below the location of the water table in the absence of a fringe, for $q/K = 0{\cdot}1$. The figures against the individual curves show values of y_{st}/a, i.e. approximations to the depth of the impermeable bed expressed as a fraction of the semi-drain separation.

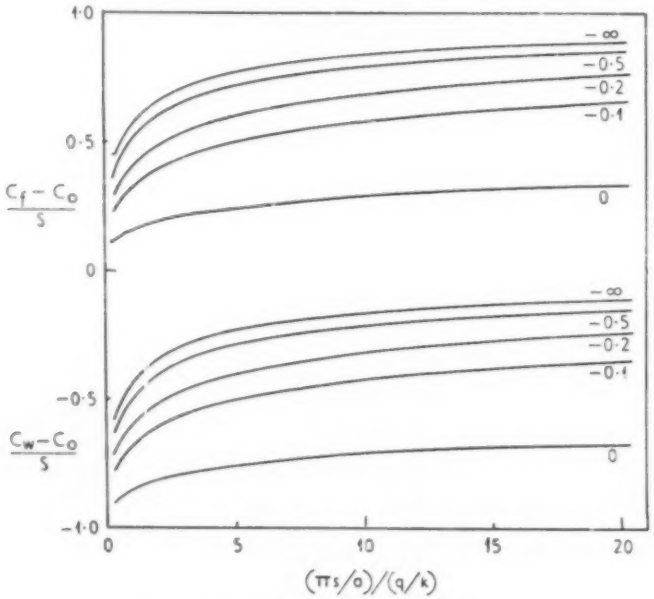

FIG. 4. As for Fig. 3, but for $q/K = 0{\cdot}01$.

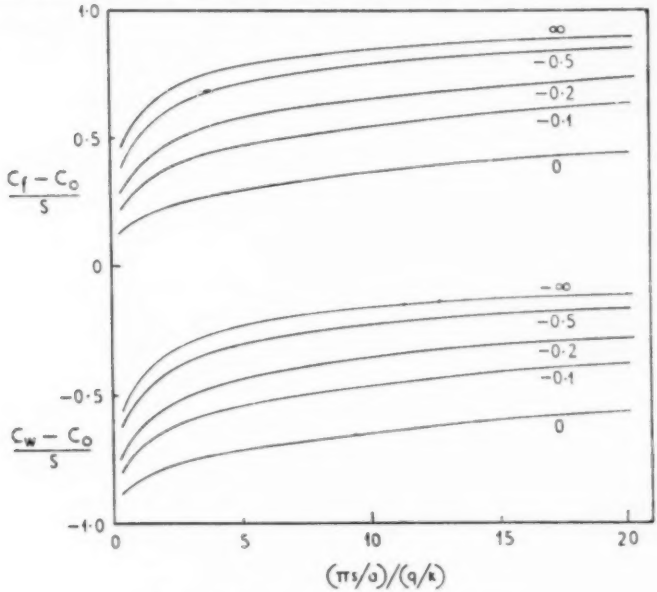

FIG. 5. As for Fig. 3, but for $q/K = 0{\cdot}001$.

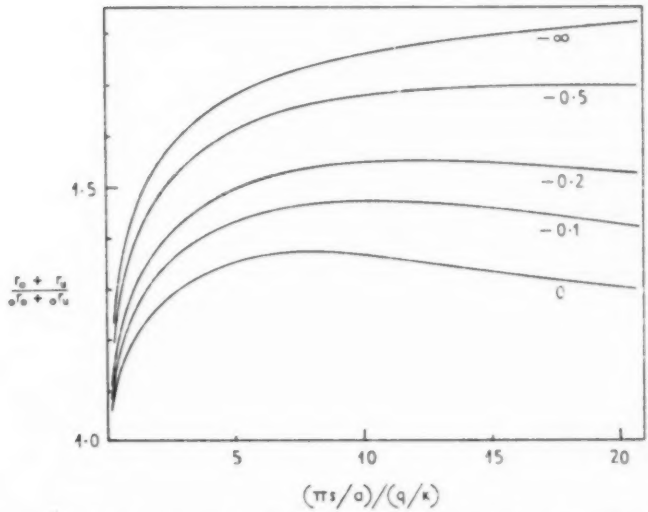

FIG. 6. Ratios of the optimum drain diameter in the presence of a capillary fringe to the optimum diameter in the absence of a fringe, for $q/K = 0{\cdot}1$. Figures against the curves show y_{st}/a.

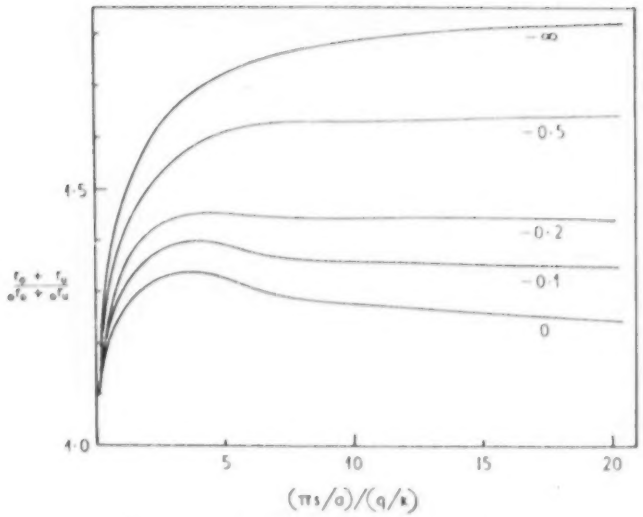

FIG. 7. As for Fig. 6, but for $q/K = 0{\cdot}01$.

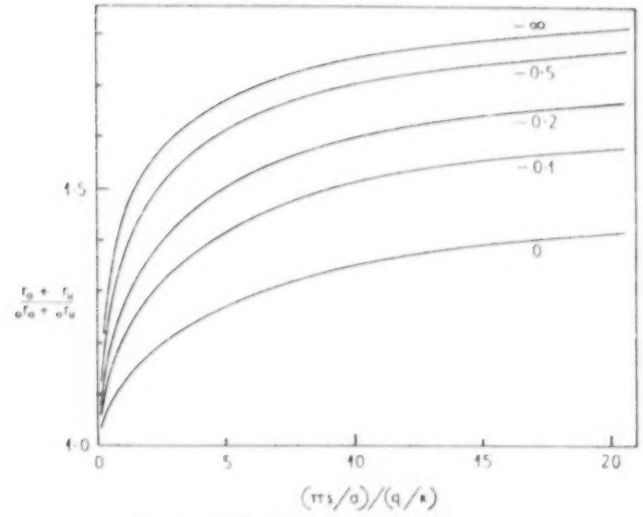

FIG. 8. As for Fig. 6, but for $q/K = 0{\cdot}001$.

shows only the ratio $r_0/_0r_0$ and in part because the greater accuracy in determining θ which is practicable with the aid of Edsac II has had an appreciable effect here.[1]

The calculations are carried through with chosen values of q/K, L/q, and $(\pi s/a)/(q/K)$ and the values of y_{st} emerge with the other results. It happens that for different values of s the stagnation point moves slightly, so that the bed depth for which c_f and c_w are calculated is not that for which c_0 is found. It was therefore necessary to plot c_f and c_w as a function of y_{st} for each value of s and to interpolate in order to find values of these quantities corresponding to the same value of y_{st} as prevailed for the calculation of c_0. The ratios $(c_f-c_0)/s$ and $(c_w-c_0)/s$ could then be determined. A further interpolation then sufficed to establish these ratios for the selected values of $(\pi s/a)/(q/K)$ indicated in the figures. Similar interpolations were made for the ratios of the drain diameters.

Discussion

The choice of values of q/K may deserve a word of explanation. If this value is unity then c_f becomes infinitely large; that is to say the soil inevitably becomes waterlogged to the surface. This value is evidently the upper limit. To take an example, the hydraulic conductivity of Gault clay at a site on the Cambridge University Farm has been found to be of the order of 1 mm. per day, so that a rainfall of this same magnitude would provide surface waterlogging. In fact the mean rainfall over a period of 2 or 3 weeks of a typical period of drainage stress in this locality is about 5 mm. per day, and it is this ratio of q/K, in excess of unity, which determines that surface water is the characteristic feature of clay land problems. Hydraulic conductivities of the order of 1 to 10 cm. per day are common in loams, and a value of q/K of 0·1 may be taken as the maximum for which under-drainage theory has a useful application. At the other extreme drainage associated with irrigation systems commonly presents low values of q/K, since the scarcity of water ensures that the application is in excess of consumptive use by only as much as is necessary to ensure the removal of salts in the drainage water. For example, at a site near Baquba in Iraq where the sandy medium loam soil had a measured hydraulic conductivity ranging about 1 m. per day the excess application was estimated to be about 1 mm. per day, giving a value of q/K of 0·001. These two values of q/K were taken as the limits for our present purposes.

The curves of Figs. 3 to 5 show very clearly that the partition of the capillary fringe does indeed depend markedly on the depth of an impermeable substratum, the more markedly the lower is the value of q/K. The most striking contrast is that between the highest and lowest values of q/K for the greatest fringe thickness and zero bed depth, i.e. the right-hand ends of curves 0 in Figs. 3 and 5. In the former case (q/K having a value 0·1) the capillary fringe is accommodated almost wholly on top of the location of the water table in the absence

[1] The author is indebted to Mr. K. K. Watson for drawing his attention to the sensitivity in some cases of optimum r_0 to errors of θ determination.

of a fringe. That is to say the saturated surface is higher than the water table in the absence of the fringe by about 90 per cent. of the fringe thickness. With q/K of only 0·001 only about 30 per cent. of the fringe thickness lies above the location of the water table in the absence of a fringe. With a q/K of 0·1 the water table itself is, of course, about ten times the height of that when q/K is only 0·001, so that the question arises as to whether the fundamental factor of importance is not so much the level of the impermeable bed relative to the drains as the height of the water table above the bed.

In the light of this observation it is necessary to return to the question of the errors involved in supposing that a stagnation point of a given depth serves for our purposes as a sufficient approximation to an impermeable bed at the same uniform depth. In so far as in the worst case (for zero bed depth and a value of q/K of 0·001) the approximation results in an over-estimate of the water-table height of the order of 50 per cent. it might be expected that the contrast in the partition of the fringe as between the cases for greatest and least q/K is under-emphasized. The matter may be put in a different way. Since for zero bed depth the height of the water table (of fringe boundary c_f) is approximately proportional to the square root of q/K (a conclusion in which the hodograph analysis concurs with the Dupuit–Forchheimer concept) a 50 per cent. increase of water-table height corresponds to an increase of q/K of about 125 per cent. One may therefore regard the curves of Fig. 5 as being, perhaps, more appropriate to a value of q/K of 0·00225 than to 0·001. A comparison with Fig. 4 for a tenfold increase of q/K will indicate that the error is not very large, but the point may be examined again in due course when the validity of the approximation has been further studied.

One further point needs to be mentioned. In every case the calculation of fringe boundary has been made for the optimum drain size, that is to say the drain for which the water table just intersects the drain roof. This drain size varies with the thickness of the capillary fringe, and consequently the values of c_f and c_w in the factors $(c_f - c_0)$ and $(c_w - c_0)$ are for one drain size and the value of c_0 is for another and somewhat smaller drain size. The magnitudes of the drain size variation are shown in the appropriate curves (Figs. 6 to 8) in this paper and in Part I. This comparison has been made in order to compare the results of the theoretical analysis with and without a capillary fringe. It may, however, be held that it is instructive to examine the partition of the capillary fringe when the drain size is held constant at, say, the optimum value in the absence of a fringe.

The consequence of allowing the drain size to increase as required to maintain the optimum condition is twofold. Firstly, since the origin of coordinates is approximately on the drain axis and the drain is regarded as just filled with water, the size increase involves a rise of level of water in the drain, an increase of hydraulic potential everywhere in the system to match this rise, and a rise of water table on this account alone. Secondly, the increase of drain size results in readier flow of water to the drain (i.e. a reduction of resistance of the system to flow)

and a lower water table as compared with the original smaller drain, although the effect is known to be small except for marked differences of drain size (Engelund, 1951). These two effects oppose each other and the net change of level of water table is not to be expected to be large. However, the question may be answered beyond doubt by making the necessary calculations for a few extreme cases within which all practical cases are likely to lie. One has simply to find, by trial and error, using

TABLE 1

			Constant drain size, optimum for s = 0		*Optimum drain size in all cases*	
L/q	q/K	$\pi s/a$ q/K	$\frac{c_f - c_0}{s}$	$\frac{c_0 - c_w}{s}$	$\frac{c_f - c_0}{s}$	$\frac{c_0 - c_w}{s}$
0	0·1	0·5	0·587	0·522	0·534	0·576
0	0·1	20	1·015	0·074	1·010	0·079
0	0·001	0·5	0·522	0·478	0·478	0·522
0	0·001	20	0·898	0·103	0·893	0·108
2	0·1	0·5	0·463	0·647	0·402	0·708
20	0·001	0·5	0·248	0·752	0·180	0·820

For each combination of parameters shown in columns 1 to 3 this table shows in columns 6 and 7 respectively the positions of the capillary fringe boundary and the water table with respect to the position which the water table would have occupied had there been no capillary fringe, the drain size appropriate to c_f and c_w being that which makes c_f least, and that appropriate to c_0 being that which makes c_0 least. For comparison, columns 4 and 5 present the corresponding values when the drain size for which c_f and c_w are calculated is the same as that for c_0, and is that which is optimum for c_0.

equations (8) and (9), a pair of values of β and δ_b which give a zero hydrostatic pressure at the same ordinate r_0 for the chosen value of s as for zero s. This will not necessarily give the same value of r_u and therefore of drain diameter, but a choice of β and δ_b to give the same diameter but not the same r_0 would not give the same zero pressure datum. Our choice is the best compromise in the circumstances.

Four cases were chosen for zero L (i.e. infinitely deep impermeable bed) with the four combinations of greatest and least q/K and greatest and least $(\pi s/a)/(q/K)$; and in the light of these results two cases were chosen for a value of L/q required to bring the stagnation point to just above drain level, these cases having least $(\pi s/a)(q/K)$ with greatest and least q/K respectively. The results show how correction of drain radius to the value for zero s affects the value of the ratios $(c_f - c_0)/s$ and $(c_0 - c_w)/s$ and are presented in Table 1. It will be seen that the differences are small, the greatest being about 6 per cent. of the capillary fringe thickness for the thinnest fringes. For the thickest fringes the differences are negligible.

Acknowledgement

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REFERENCES

CHILDS, E. C. 1959. A treatment of the capillary fringe in the theory of drainage. J. Soil Sci. **10**, 83–100.

DEEMTER, J. J. VAN. 1950. Theoretische en numerieke behandling van ontwaterings-en infiltratie-stromingsproblemen. Versl. Landb. Onderz. No. 56.7, 1–67.

ENGELUND, F. 1951. Mathematical discussion of drainage problems. Trans. Dan. Acad. Tech. Sci. No. 3.

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EFFECT OF DRAINAGE ON CERTAIN PHYSICAL PROPERTIES OF A HEAVY CLAY SOIL

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Summary

Comparisons of the physical properties of a drained and undrained heavy clay soil revealed a higher content of water-stable aggregates, a higher proportion of larger pore spaces and a greater vertical and lateral hydraulic conductivity in the former. The difference generally decreased with depth; at about 15 in. there was generally little difference between the two soils. Despite possible initial differences in texture, the difference can be interpreted as being largely due to the effect of drainage on aeration.

Introduction

In 1954, in order to assess the effect of draining a heavy clay soil on the establishment and growth of trees, the Forestry Commission Research Branch laid out an experiment in an area over Oxford Clay, in the region of Waterperry, Oxon. (Bernwood, Expt. No. 1). Following the removal of the original hardwood scrub cover and burning, three intensities of draining were introduced: (1) controls—shallow drains designed only to prevent surface waterlogging, (2) drains, 2 ft. deep, spaced 1 chain apart, and (3) drains, 2 ft. deep, spaced ½ chain apart. The area was then planted to a variety of tree species. Subsequent observations on bore holes (Fourt, 1960) confirmed that during winter and early spring, standing water-levels in the drained plots were appreciably lower than in the controls; during the summer, however, at least in the wetter years 1956 and 1957, the situation was reversed, with indications of higher water-levels in the drained plots. Experiments with fluorescein dye suggested that in winter lateral movement of water in the drained soils occurred at deeper levels than in the controls.

The following is an account of a more detailed investigation made in 1959 into certain physical properties of soils from the control and most intensively drained plots. Table 1 gives morphological descriptions of profiles representative of a number of pits dug in the two areas.

TABLE 1

Morphology of Soil Profiles

Control	*Drained*
0–1·5 in. Very dark grey-brown loam (10 YR 3/2); fine granular structure; loose; friable; moderately high organic-matter content;[2] non-calcareous;[2] roots abundant; few earthworms; no apparent mottling.	0–1·5 in. Very dark grey-brown loam (10 YR 3/2); fine granular structure; loose; friable; moderately high organic-matter content; non-calcareous; profusely permeated by a dense mass of roots; many earthworms; no mottling.

[1] Forest Research Institute, Dehra Dun, India.

[2] From subsequent laboratory tests.

1·5–6·5 in. Dark grey-brown loam (10 YR 4/2); crumb to cloddy structure; loose; friable tending to become hard and coherent below; moderate to low organic-matter content; non-calcareous; numerous roots but decreasing downwards; few small dark concretions present (MnO_2); few earthworms; fairly distinct pale brown mixed with grey mottling on root channels and structural faces.	1·5–7·0 in. Dark grey-brown loam (10 YR 4/2) tending to yellow-brown (10 YR 5/4); crumb structure; loose; friable; moderate to low organic-matter content; many roots but less abundant than in the upper layer; non-calcareous; few small dark concretions (MnO_2); many earthworms; poorly developed brown stains of iron oxide on the interfaces of the structural elements and on the root channels.
6·5–11·0 in. Dark yellowish-brown clay loam (10 YR 4/4) to grey-brown (2·5 Y 5/2); proportion of clay increasing with depth; crumb to columnar structure; comparatively harder and more compact; low organic-matter content; non-calcareous; very few live roots; old dead roots more common; few small black concretions; very few earthworms; smell of H_2S; very prominent coatings of pale-brown and bluish-grey colour on the structural elements.	7·0–12·0 in. Dark yellowish-brown clay loam (10 YR 4/4) tending to dark brown (10 YR 4/3); crumb to cloddy structure, soft friable tending to be coherent and compact below; low organic-matter content; non-calcareous; live roots frequent but less prominent; old dead roots present; few small black concretions; occasional earthworms; distinct ochreous mottling mixed with coatings of bluish grey.
11·0–14·0 in. Dark grey-brown clay (2·5 Y 4/2); columnar to massive structure; very hard and compact; coherent and plastic; very low organic-matter content; non-calcareous; few oyster shells of *Gryphaea dilatata*; small black concretion of MnO_2, conspicuous smell of H_2S; mottling of pale brown and bluish grey, but bluish grey becoming more prominent; roots rare.	12·0–15·0 in. Grey-brown clay (2·5 Y 5/2); cloddy to columnar structure; coherent; fairly compact; very low organic-matter content; non-calcareous; few live roots; dead roots present; frequent brownish-black nodules of manganese dioxide; earthworms present; strong reddish-brown mottling with the proportion of bluish grey increasing downwards.
Below 14·0 in. Dark grey clay (5Y 4/1); massive structure; extremely hard and indurated; very low organic-matter content; non-calcareous; very strong smell of H_2S; faintly developed brownish-yellow markings; structural faces almost entirely coated with bluish-grey mottling; old dead roots; live roots rare.	Below 15 in. Dull grey clay (2·5Y 4/2); columnar structure; coherent; compact; very low organic-matter content; non-calcareous; few live rootlets but many old dead roots; few oyster shells of *Gryphaea dilatata*; prominent yellowish-brown spotting associated with bluish-grey mottling; bluish-grey coating more prominent; feeble smell of H_2S.

Experimental

Sampling

To allow for heterogeneity in the soils over the areas examined, separate samples were taken from each of six pits, dug to a depth of about 2 ft., in each of the control and drained areas. The pits in each area were spaced about 12 ft. apart and were located midway between trees to avoid the effects of planting disturbances. For measurements on lateral

hydraulic conductivity, undisturbed samples were taken from the sides of the pits at four depths (1½–4½, 5½–8½, 9½–12½, and 13½–16½ in.) using the sampling tube and inner tin liners (3 in. diameter, 2 in. high) described by Low (1954). Following the removal of the liners from the tube, the soil was carefully trimmed flush at both ends and covered with tightly fitting lids. For measurements on water-stable aggregates, pore-space distribution and vertical hydraulic conductivity, duplicate samples were collected using the same apparatus, by successively cutting steps in the sides of the pits and sampling vertically at four depths (1½–3½, 5½–7½, 9½–11½, and 13½–15½ in.). For mechanical analyses, samples were taken at the same four depths from two pits in each of the control and drained areas.

Methods and Results

Mechanical analysis

The standard Bouyoucos hydrometer method was used, with NaOH as the dispersing agent. The mean values are given in Table 2.

TABLE 2

Average Mechanical Composition of Control and Drained Soils

	Control			*Drained*		
Depth (in.)	*% sand*	*% silt*	*% clay*	*% sand*	*% silt*	*% clay*
1·5–3·5	45	22	34	57	17	26
5·5–7·5	41	17	43	51	15	35
9·5–11·5	28	14	59	47	10	43
13·5–15·5	28	13	59	45	6	49

Water-stable aggregates

The method used for wet sieving was essentially the same as that described by Low (1954) except that four sieves of 4, 2, 1, and 0·5 mm. mesh were employed. The means of the six samples are represented in histogram form in Fig. 1.

Hydraulic conductivity

The apparatus, designed independently for this investigation, proved to be similar in principle to that described by Andersson (1955) (cf. Plate I). Each unit consisted of a cylindrical copper vessel (4 in. I.D., 3 in. high) surrounded at the top by a 1-in. deep channel, the outer rim of which was about ½ in. above the inner rim. This outer channel was inclined at a slight angle to facilitate drainage through the copper tube outlet. After removing the two lids of the tin containing the soil core, the bottom was covered by a filter paper which was kept in place by a thin rubber band. The soil was then saturated from below by standing in a bowl of water; evacuation in a vacuum desiccator proved necessary to saturate samples from the lower horizons. The sampling tin with

saturated core was then placed inside the copper vessel, on a raised perforated copper plate such that the upper surface of the core was about ¼ in. below the top of the inner wall. By means of a rubber sleeve, the container was coupled at the top to a similar, but empty container,

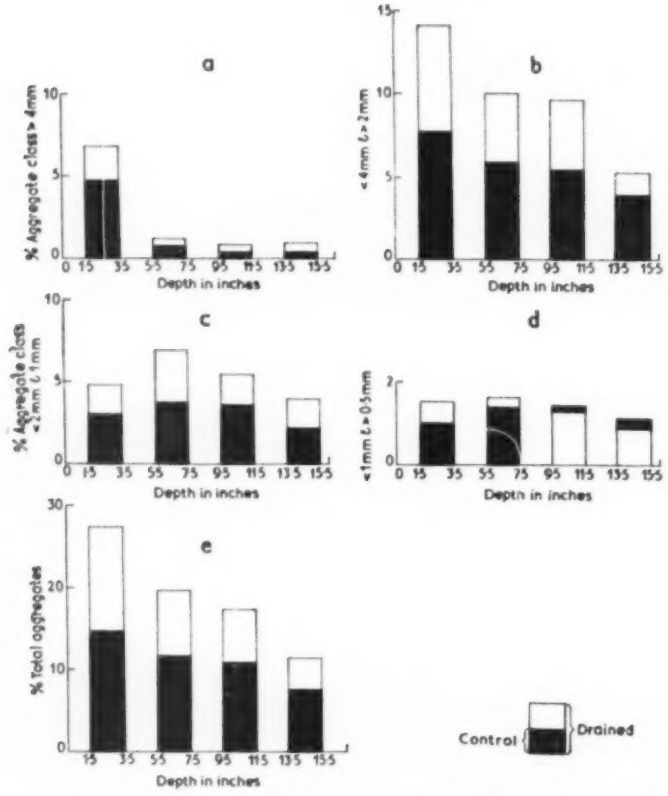

FIG. 1. Mean percentage water-stable aggregates in control and drained soils at different depths.

a > 4 mm., *b* < 4 mm. > 2 mm., *c* < 2 mm. > 1 mm., *d* < 1 mm. > 0.05 mm., *e* Total.

provided with ¼ in. copper inlet and outlet tubes. To minimize disturbance, a filter paper was placed on the upper surface of the soil core.

The whole apparatus consisted of eight such units with the upper containers connected in series by polythene tubing, thus allowing eight soil samples to be investigated simultaneously. Before beginning the experiment, the copper vessels were completely filled with water, any excess running over the top into the channel being discarded. A continuous and gentle stream of water was then passed through the upper

containers, maintaining, in each unit, a constant head of water (just under 2 in.). Percolate passing downwards through the core displaces an equal volume of water into the outer channel which, after a suitable time interval, can be collected and measured.

Hydraulic conductivity was calculated using D'Arcy's equation. The means of the six samples are represented in histogram form in Fig. 2.

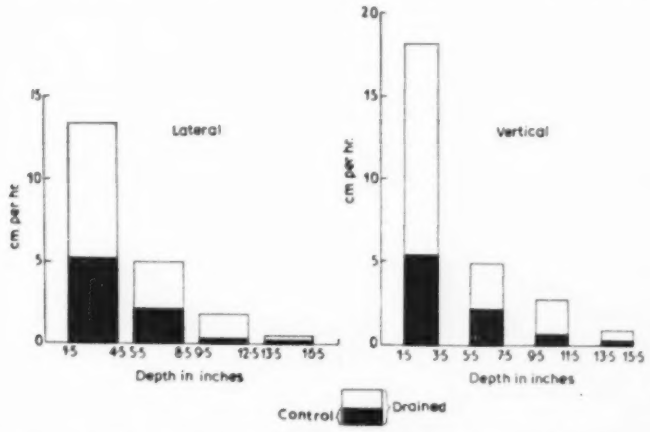

FIG. 2. Mean lateral and vertical hydraulic conductivities in control and drained soils at different depths.

Pore-space relations

The same soil used for the determination of vertical hydraulic conductivity was used for pore-space determinations. The saturated core was weighed along with the container and filter paper and placed on the sintered glass base (porosity 4) of a Buchner funnel. The soil was pressed gently on to the base to ensure good contact and the top of the funnel covered with polythene sheet to prevent evaporation. The funnel was connected via a 500-ml. filter flask and trap bottle to a filter pump and water manometer.

A number of samples were subjected initially to tensions of 45, 75, and 130 cm. water and the amount of water released at each tension determined from the loss in weight. However, as there appeared to be little difference between the soils at higher tensions, subsequent investigations were confined to the 45 cm. tension. After draining and weighing and allowing for the weight of the extra items and the water taken up by the filter paper, the amount of air-filled pore space at this tension could be calculated in terms of the total volume of the soil core. Allowing for the height of the soil sample above the water in the flask and a certain amount of fluctuation, the actual tension lay between 44 and 48 cm. water. The means of the six samples, together with their standard errors, are given in Table 3.

TABLE 3

Mean Percentage Air-filled Pore Space in Control and Drained Soils at 44–48 cm. Water Tension

Depth (in.)	*Control*	*Drained*
1·5–3·5	7·6 ± 0·5	12·8 ± 1·0
5·5–7·5	6·3 ± 0·4	10·0 ± 0·3
9·5–11·5	3·9 ± 0·3	7·7 ± 0·6
13·5–15·5	2·4 ± 0·3	5·5 ± 0·2

Discussion

Whilst both soils reveal an increasing clay content with depth (Table 2) there is evidence that the drained soil contains a consistently lower silt and clay content at all depths. Since it is hardly likely that this difference could have been entirely brought about by a greater rate of eluviation of the finer particles in so short a time, it would appear that the soils in the two areas differed initially in texture. Though two samples from each area are insufficient to establish the extent of soil heterogeneity in the area as a whole, the possibility of an initial difference in texture must be borne in mind when interpreting differences in other physical properties apparently brought about by draining.

Fig. 1 clearly indicates the greater degree of soil aggregation in the drained soils, and considering the relatively coarser texture of these soils there can be little doubt as to the positive effect of drainage on this property. In both soils the larger the aggregate class the more rapid does the percentage content fall with depth; this would be expected if aggregation is largely a result of microbial and faunal activity in the better aerated upper layers of the soil. Also with increasing depth, for all size classes (with the possible exception of the largest aggregates), the difference between the two soils decreases so that at the lowest depth sampled, and for the smallest aggregates, there is probably little difference between the two: again this may be interpreted largely through the influence of drainage on aeration, the effect decreasing with soil depth. The somewhat different picture presented for the largest aggregates, suggesting an influence of drainage only in the uppermost horizon, may be due to the overwhelming influence of rooting in this region, though, because of the particular technique employed, it is probably unwise to lay too heavy a stress on this conclusion. At the same time, differences in the moisture régime of the two soils may also be involved. Destruction of aggregates in soils of high clay content following wetting has been ascribed by Low (1954), Brewer and Blackmore (1956), and others, to swelling of the constituent particles, and the more violent fluctuations in the moisture content of the undrained soils may perhaps be a contributory factor.

Consistent with its effect on aggregation, there is an undoubted effect of drainage in increasing the percentage of larger pores and hence the content of air-filled pores at the particular tension applied (Table 3.) The observation that in both soils the proportion of air-filled pores

decreases with depth reflects the dependence of this property on the content of stable aggregates and the factors responsible for their formation or destruction.

Since hydraulic conductivity is a function of soil porosity and the size distribution of the pores, the findings on this property (Fig. 2) generally bear out the results for aggregation and pore-space relations. As Nelson and Baver (1940) have already shown, the amount of water released by a soil at a tension of 40 cm. water gives a very good relation with permeability. Despite the possibility of textural differences, there is an undoubted influence of drainage in increasing both vertical and lateral components and, as with most other properties examined, the effect falls off with depth. The vertical component is consistently greater than the lateral component, in agreement with previous findings (Childs *et al.*, 1957), no doubt largely because of the vertical orientation of structural faces, of root penetration and of faunal activity.

Conclusions

Generally speaking, the results have largely confirmed expectations based on previous experience, though the precise quantitative effect of drainage cannot be assessed in this case because of possible initial differences in the texture of the soils from the two areas sampled. There is, however, no doubt that, independent of this factor, drainage has resulted in a significant increase in the content of water-stable aggregates, in the proportion of larger sized pores, and in both vertical and lateral components of the hydraulic conductivity. This effect generally decreases with soil depth and at the lower depths sampled there was usually relatively little difference between the two soils other than that which can perhaps be accounted for by differences in texture.

Primarily the drainage effect can be interpreted in terms of the better conditions of aeration of the soil and the effect of this on rooting, microbial and faunal activity; the difference is clearly revealed in the morphology of representative profiles, especially in the depth and intensity of gleying. At the same time there is perhaps some reason to believe that the different moisture régimes of the two soils is also of significance. Since waterlogging has often been reported as causing deterioration in soil structure, the undrained soil would be expected to possess a poorer structure than the drained.

Despite the considerable attention paid to drainage of heavy soils, there is surprisingly little quantitative data as to its effect on physical properties, and the results of the present investigation, based on relatively simple laboratory techniques, may therefore be of some interest. Nevertheless, it is evident that despite the number of replicate samples investigated and the general consistency of the findings, the heterogeneity of the soil in this particular area is such that a much more thorough sampling would be necessary to determine the precise quantitative effect of draining. For this reason it would probably be unwise to speculate too much on causal relations.

REFERENCES

ANDERSSON, S. 1955. Physical studies on cultivated soil. VIII. An experimental method. Grundförbättbring, **8** (2), 98.

BREWER, R., and BLACKMORE, A. V. 1956. The effects of entrapped air and optically oriented clay on aggregate breakdown and soil consistence. Aust. J. Appl. Sci. **7**, 59–68.

CHILDS, E. C., COLLIS-GEORGE, N., and HOLMES, J. W. 1957. Permeability measurements in the field as an assessment of anisotropy and structure development. J. Soil Sci. **8**, 27–41.

FOURT, D. 1960. Report on Forest Research, 1959. H.M.S.O. London.

LOW, A. J. 1954. A study of soil structure in the field and the laboratory. J. Soil Sci. **5**, 57–74.

NELSON, W. R., and BAVER, L. D. 1940. Movement of water through soils in relation to the nature of the pores. Soil Sci. Soc. Amer. Proc. **5**, 69–76.

(*Received 18 December 1959*)

Apparatus for hydraulic conductivity determinations.

1, 2, 3. Sampling tin with lids.
4. Soil core in tin with filter paper.
5. Upper tin with inlet and outlet tubes.
6. Rubber sleeve. 7. Perforated plate.
8. Copper vessel with outer channel.
9. Complete unit.

Apparatus for hydraulic conductivity determinations. Series of eight complete units.

L. LEYTON AND J. YADAV—PLATE I

WATER CONTENT AND SOIL STRENGTH

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Summary

The strength of beds of soil aggregates, saturated and unsaturated, has been measured with a ring shear machine. For saturated loose soil with free drainage the cohesion and friction components and, therefore, total strength are proportional to the applied normal load. When sheared under load the soil compresses to an ultimate voids ratio after which there is negligible change. This ultimate state differs from the critical voids ratio for saturated clay in that it appears to depend on the strength of the individual aggregates as well as on the nature of the soil material.

In unsaturated soil, as the aggregates are strained, suction in the pore water increases. This suction acts as an equivalent applied load on the water-filled fraction of the soil, and increases its potential resistance to strain by an amount determined by the apparent coefficient of friction of the saturated soil. The ultimate voids ratio for the unsaturated soil at any load is higher than that for the saturated soil.

I. *Introduction*

THE shear and compressive strength of loose soil is important in agriculture both in maintaining soil structure against compaction by animals and farm machinery and in determining the specifications of cultivation implements designed to change the structure of the soil. There is also wide interest in soil strength in the engineering field where stability under roads in earth dams and embankments is important. The strength of a cultivated soil is related to its water content and other factors and the lack of information about this relation limits the usefulness of strength measurements. Compaction tests on unsaturated soil are made over a range of water contents at arbitrary rates of loading and with unknown amounts of shear force. Their application is restricted.

In 1948 Bodman and Rubin described a ring shear machine for compressing and shearing loose beds of soil. They suggested the term 'soil puddlability' to describe the tendency of the soil to compress; it is numerically the inverse of soil strength (Greacen, 1959) or the load the soil structure will support without any further compression. They showed that puddlability varied greatly with water content. Other workers in agricultural engineering (Nichols, 1932; Soehne, 1958) have developed different testing techniques, and have arrived at the same general conclusions without clarifying the effect of water content.

In the field description of soils Butler (1955) has proposed a scheme for specifying soil strength based on the final degree of plasticity and on the rate at which this is attained when the soil is manipulated in a wet condition. Brewer and Blackmore (1956), using a ring shear machine designed by the present author after that of Bodmin and Rubin, showed that Butler's clays did compress at different rates when tested at an arbitrary

wetness. In every instance quoted above the work has concerned some function of the shear strength of loose soil complicated by the effect of the soil water.

Theoretical

Theoretical soil mechanics is able to handle competently the strength of saturated ideal clays, including the 'quasi-saturated' case where the

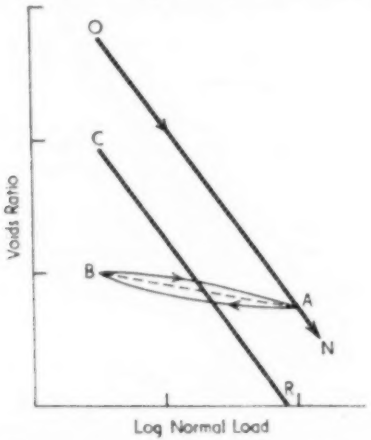

FIG. 1. Diagrammatic representation of normal consolidation curve *ON*, with unloading and reloading hysteresis loop, *AB–BA*, for an ideal saturated clay. *CR* is the critical voids ratio line obtained by shearing the compressed clay until there is no further change in volume.

water is under low suction (Aitchison, 1957). This situation has existed from the time of Hvorslev's work in 1937. Hvorslev showed that shear strength in a saturated clay was determined by two factors, firstly by the effective normal load which, with the coefficient of friction, gives the frictional shear strength or resistance, and secondly, by the voids ratio which determines the cohesion component of shear strength. Voids ratio is the ratio of the volume of pores to the volume of solids and is used here as an index of particle spacing. In a saturated soil it is also an expression of the water content. If clay is being compressed for the first time from an initial slurried condition (a process referred to usually as 'normal consolidation of virgin clay') the voids ratio is determined by the applied load and so the total shear strength is ordinarily proportional to the load. Where the soil has been previously compressed with a load that is greater than the present test load, the soil is said to be overconsolidated. In this case the voids ratio, and so the cohesion, is determined by the equivalent pressure on the normal consolidation curve as shown in Fig. 1.

In 1954 Croney and Coleman found that when a clay was disturbed mechanically a unique relation occurred between the suction and the water content. This occurred regardless of whether the condition of the

clay before disturbing was arrived at from an initially slurried condition, when the structure was partially destroyed, or from the clay in its natural state. This concept of Croney and Coleman and Hvorslev's results on shear strength were more fully developed recently by Roscoe, Schofield, and Wroth (1958) to cover changes occurring in the water content or voids ratio and the strength of saturated soil yielding under load. They demonstrated the existence of a critical voids ratio (CVR) versus load relation for clays and silts under conditions similar to those used in standard tests on soil strength. They call the plot of this relation the CVR line, the name being taken from Casagrande's work (1938) which describes the equilibrium volume for sand failing under different loads. Roscoe *et al.* plotted voids ratio against the logarithm of pressure in the standard way as shown in Fig. 1, where *OAN* is the normal consolidation curve for a virgin clay and *AB* and *BA* the unloading and reloading curves with the characteristic frictional hysteresis loop for saturated clay (Holmes, 1955). This plot is similar to Croney and Coleman's pF versus water-content plot (see their fig. 5), where the logarithm of the suction in centimetres of water, pF, is plotted on the vertical axis. Roscoe *et al.* predicted that as the saturated clay, at any voids ratio, is strained, either a suction or a positive pressure will develop in the soil water which, if the volume is held constant, will tend to change the effective normal load to that described by the CVR line. The shear strength of the clay will be determined by this new effective load and the coefficient of friction as described by Hvorslev.

Roscoe and his co-workers found for cases of high overconsolidation, i.e. where the voids ratio is relatively much lower than the equilibrium voids ratio for the test load, that the equilibrium voids ratio was not reached but that the sample tended to fail in a plane rather than strain throughout uniformly. This means in effect that on straining, strong clays tend to break down into smaller aggregates.

Application to agricultural soil

In the present work an attempt has been made to apply the above hypothesis for saturated clay to agricultural soil. Such a soil may be considered as a bed of overconsolidated aggregates, the degree of overconsolidation being related to the extent of drying which the aggregates have previously experienced (Aitchison, 1957). When wetted up the voids ratio and so the strength of the individual aggregates will be determined in part by the extent of swelling. If a saturated bed of aggregates is sheared under a normal load a certain amount of aggregate disruption will occur (Greacen, 1957) depending on the aggregate strength and the load used. Taking the extreme theoretical case where the aggregates are strong enough to resist any disruption at the normal load used, a critical voids ratio should develop similar to that for a bed of sand. Experimentally this CVR for sands when saturated will be difficult to obtain, since the final state of the sample will require an expansion which will tend to cause failure in one plane. For weakly aggregated soils, if complete disaggregation occurs, a critical voids ratio might be obtained which will be characteristic of the ultimate clay particles. Between these

two extremes of aggregate strength it is possible that a fraction of the aggregated soil will be broken down, particularly at contact points, until a balance is reached between the strength of the remaining aggregates and the strength of the whole bed. This bed strength will be determined by the coefficient of friction and load. A critical voids ratio should be obtained experimentally which is characteristic of the aggregate strength. Further, since the sample compresses uniformly throughout, the ultimate strength of the bed should correspond to the maximum strength at failure.

In the case of unsaturated soil the individual clay aggregates are saturated with water even at water contents as low as the wilting point (Holmes, 1955). The strength of these overconsolidated aggregates will be determined by the voids ratio and the effective load described by Fig. 1. If the aggregate is now strained the suction might be expected to adjust as described by Croney and Coleman. This resulting change in suction in the water will be expected to apply an equivalent load over and above the applied mechanical load so that the effective load versus water-content plot will approach an equilibrium line depending on the extent to which the aggregates are broken down. Provided sufficient contact can be made with the straining soil so that some conductivity exists, it should be possible to measure the suction by means of a tensiometer.

Investigation of these points of interest involves controlled continuous strain, and, since we are dealing with normal consolidation and shear of a bed of overconsolidated aggregates, degrees of strain much greater than can be obtained with the standard box or triaxial strength testing machines. Furthermore since we are dealing with equilibrium or ultimate states any time-dependent factors must be avoided where possible. Thus the maximum rate of strain should be determined by drainage rates in saturated testing and in unsaturated testing by the response time of the suction-measuring device.

II. *Experimental Methods*

Strength apparatus

The apparatus was a ring shear machine with a controlled rate of shear similar to that of Bodman and Rubin but capable of being operated at very much lower rates of strain. In contrast to their machine both the shearing and the compression loads were applied from above through the drive shaft of the piston (see Plate I). This avoided loss of normal load through friction.

The drive shaft was held upright by two plain bearings set 6 in. apart in the top plate of the frame. The drive mechanism was mounted directly on top of the drive shaft and formed part of the compression load. It consisted of two small 24-volt electric motors and the gearbox of a compass-correcting device coupled through the gearbox of an aircraft propeller-feathering mechanism. This gave a linear testing speed of 0·043 cm./min. at the mid-point of the annular sample. The normal load on the soil was varied by counterbalancing the total load of the piston and drive mechanism through an overhead pulley system.

The torque caused by the resistance of the soil to shear was transmitted through the drive shaft to the casing of the lower gearbox. This was prevented from turning by two balanced tension bars. The total turning moment was measured as a deflexion in the tension bars by means of two dial gauges. Friction on the contact points of the tension bars was overcome by means of small ball races. Side thrust in the main drive shaft bearings was avoided by mounting the tension bars directly opposite each other. Average shear stress was calculated from the measured moment M (g.cm.) according to Hvorslev (1939):

$$S = \frac{3M}{2\pi(R_2^3 - R_1^3)} \qquad (1)$$

where S is the shear strength (g./cm.^{2}) and R_2 and R_1 are the external and internal radii of the ring-shear cylinder 7 cm. and 4 cm. respectively. Divisions of 10^{-3} in. on the dial gauges corresponded to shear strength values of 2 g./cm.^{2}. For compression loading when the piston and drive mechanism were counterbalanced, loads of 2 g./cm.^{2} were sufficient to cause the piston to move on to the soil. The volume of the sample could be obtained at all times from the change in height of the sample by means of a second 0·001 in. dial gauge. For a typical test, where 0·5 cm. depth of solids was used, with a voids ratio of 1·0, 0·001 in. change in sample height corresponded to a voids ratio change of 0·005.

Measurement of soil water suction

The effective soil water suction was measured by means of a null point tensiometer. This consisted of a ceramic cup (wall thickness $\frac{1}{16}$ in.) which was machined to form the inside wall of the annular shear cylinder (see Plate I). The cup was connected through a 0·25-mm. bore capillary tube with bubble to a variable mercury manometer. Any change in the suction during testing was noted by a tendency for the bubble to move towards or away from the tensiometer, and this was corrected manually by changing the balancing pressure in the manometer by means of a metal bellows. As the working area of the tensiometer was about 25 cm.^{2}, 1 cm. movement of the indicating bubble corresponded to a movement into or out of the soil of a depth of 2×10^{-8} cm. of water (ignoring the voids ratio correction) so that suction was measured virtually without disturbing the soil water condition.

The reaction of the tensiometer was fast enough to follow the changes in suction resulting from the slow rate of strain used in the tests. For the soil wetness described here, when the straining ceased at a maximum shear strength, there was no significant change in the tensiometer reading over a period of several days. For a theoretical treatment of null point tensiometers the reader is referred to a paper by Miller (1951).

Testing procedure

The results reported here were obtained on the 0·7–1·4 mm. aggregate fraction of two clays, some physical properties of which are given in Table 1. The subsoil of the Urrbrae loam has a weak structure. It will

TABLE 1

Soil Physical Data

Soil	*Mechanical analysis*•				*Atterberg limits*		
					Lower plastic limit		
	% *Coarse sand*	% *Fine sand*	% *Silt*	% *Clay*	% *dry wt.*	*vol. liquid* / *vol. solid*	*Liquid limit* % *dry wt.*
Plastic clay .	1	7	23	72	24·1	0·66	78
Stable clay .	3	12	51	38	41·8	1·12	83

• Mechanical analysis without organic-matter digestion. The stable clay gave higher clay content with increased mechanical stirring.

be referred to as the plastic clay. It is quite plastic when wet; the aggregates slake readily in water giving small aggregates (approx. 50 μ) which do not disperse. On the other hand, the Wollongbar loam, a krasnozem, has a very strong structure; it becomes plastic only after prolonged working and has high aggregate stability to all water treatments. It will be referred to as the stable clay. The aggregate fraction was obtained by dry sieving. It was wetted up to the desired water content by means of a fine spray of water, thoroughly mixed, and allowed to stand for one week in a sealed bottle at 20° C. Samples containing the equivalent of about 50 c.c. real volume were packed uniformly into the cylinder of the shear apparatus. The cylinder was then mounted in position under the piston, and the soil volume gauges set to the initial volume of the sample. While the cylinder was being assembled under the piston the manometer reading was brought into equilibrium with the initial water suction. For saturated tests the soil was packed under water: the outer ring of the cylinder was sealed to the base with light grease, the cylinder was partly filled with water and the wet aggregates poured into the water and levelled.

During tests on saturated soil excess water drained away either from under the cylinder walls, up past the piston, or through the tensiometer, so that maximum length of the drainage path was approximately 1·5 cm.

The actual strength testing proceeded in two stages:

(*a*) *Normal compression.* The required normal load, which ranged from 150 to 850 g./cm.^{2} for these tests, was applied by adjusting the load on the piston as described above. The soil was allowed to compress under the constant load for a period of 30 min. when, owing to the high permeability of the aggregate bed compared, for example, to that of a slurried clay, the rate of strain was negligible (less than 0·0001 in./min.). The plot of the voids ratio at this stage against the applied load, P, was taken as the normal consolidation curve for the bed of aggregates.

(*b*) *Compression and shear.* Following normal compression the motor was turned on and readings taken of shear strength, voids ratio (normal strain), and suction. These values were plotted against the angular displacement in degrees of the piston relative to the cylinder, i.e. the shear strain. Shear strength, S, has been taken directly from the maximum

value recorded for M, using equation (1), and e_u, the ultimate voids ratio, as the average voids ratio of the whole sample when there was no further appreciable change in the height of the sample. This ultimate voids ratio was reached at the time of, or shortly after, maximum strength, except where drainage was limiting. Similarly the water suction recorded by the null point tensiometer has been used as the effective water suction at failure. Although each of these values is an approximation to some extent, the overall description of the stress–strain relation which they give appears to be satisfactory.

III. *Results and Discussion*

Typical stress–strain curves for the two clays are shown in Fig. 2*a* and 2*c* for the saturated tests and in Fig. 2*b* and 2*d* for the unsaturated tests. These curves represent the complete set of data for any one test.

There appear to be two stages in the development of the maximum shear strength. Initially there is a rapid compression when the shear force is applied showing that the structure in equilibrium with a pure compression force is unstable to shear. This is accompanied by a corresponding increase in shear resistance. Following this in some tests there is a slight drop in shear resistance or in others a flat section followed by a gradual increase up to a maximum shear strength. This maximum strength is accompanied by a virtually constant voids ratio which we have called the ultimate voids ratio. Under equilibrium conditions which will be discussed later it is analogous to the critical voids ratio for saturated clay.

Examination of the sample during testing showed that the soil was straining uniformly throughout except in a small region against the inner and outer walls of the cylinder. Planes of failure after testing were not perpendicular to the axis of the sample but conformed to ideal behaviour as predicted from a Mohr's diagram treatment. In the case of the plastic clay after maximum strength was reached the soil often continued to strain throughout with depth. In the case of the stable clay with continued shearing planes of failure developed parallel to the face of the piston. This final condition indicated that the soil had work-hardened to its maximum strength for the particular normal load. Any further normal straining beyond this point required an increase in the compression load. As the soil is compressing and increasing in strength up to failure, any area in the soil sample will be required to carry the full normal load so that the voids ratio of the whole sample might be expected to come to the ultimate voids ratio. The structure then possesses the equilibrium or ultimate strength for this loading.

(*a*) *Saturated soil: shear strength*

The slow build-up in the shear strength of a bed of aggregates with continued strain contrasts with the behaviour of either sands or ideal clay where the maximum shear strength and failure are reached more quickly and the drop in shear strength after failure is quite pronounced. Hvorslev found the same behaviour with the silty Vienna clay which

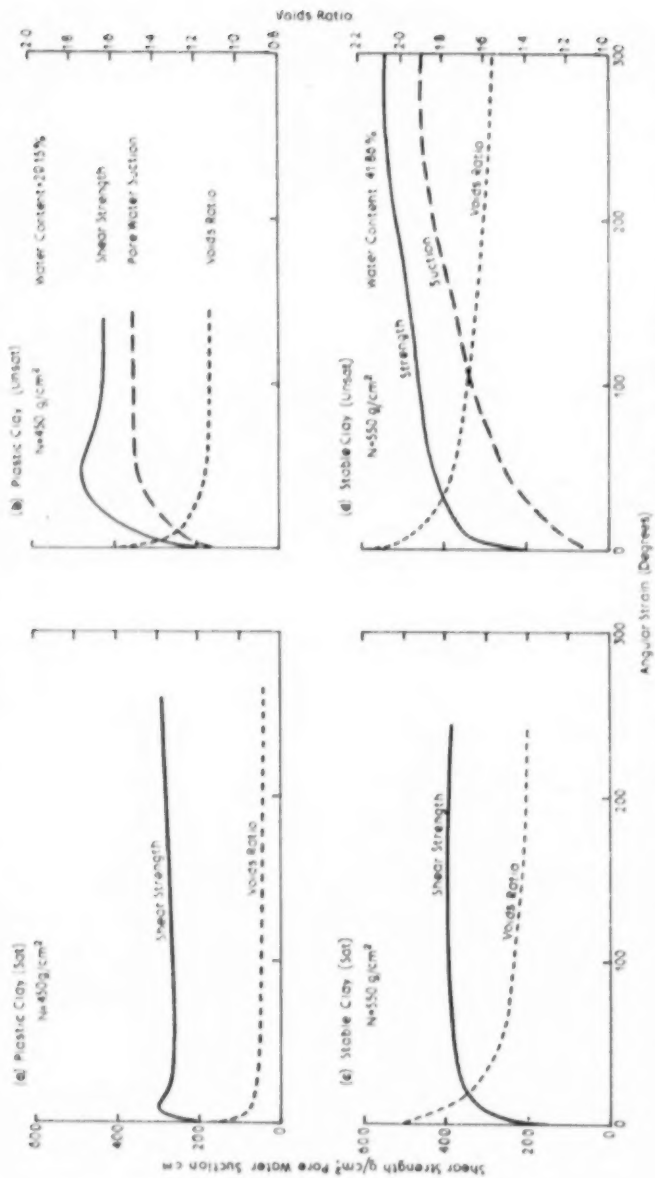

FIG. 2. Shear strength versus strain curves for saturated (*a* and *c*) and (*b* and *d*) soils. Voids ratio and, in the unsaturated case, suction in the soil water, are also given as a function of angular strain.

needed linear shear strain of the order of 12 in. in a ring shear machine of dimensions close to the present one.

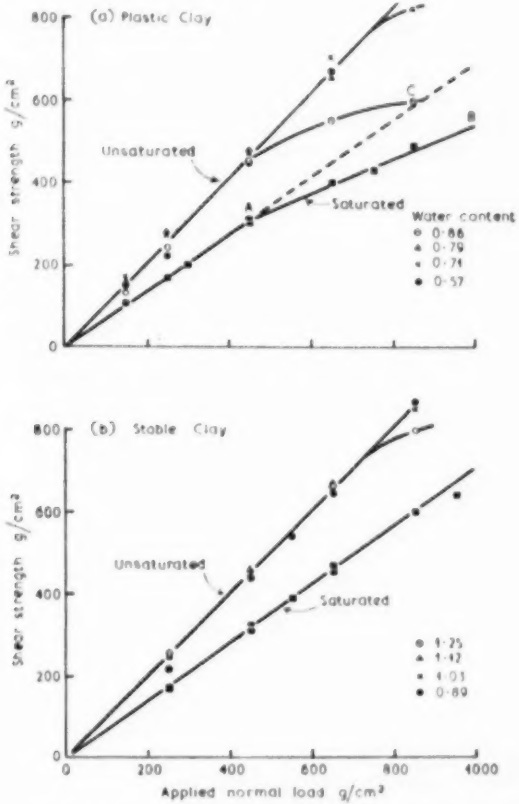

FIG. 3. Maximum shear strength versus applied load for (*a*) plastic clay, and (*b*) stable clay, for saturated and unsaturated conditions. Water content for the unsaturated soil is given as volume of water per unit real volume of solids.

In Fig. 3 *a* and *b* the maximum shear strength for the two soils in the saturated condition is plotted against the applied normal load. There are several points of interest:

(i) At low loads, for the rate of shear used, the relation between shear strength and applied load is linear. Although this is a cohesive material the loose bed of aggregates behaves as a virgin or unconsolidated clay and at zero applied load does not show any cohesion. The curve passes through the origin and the shear strength is given by the simple friction equation:

$$S = P\tan\phi_s \qquad (2)$$

where ϕ_a is the angle of apparent internal friction and as measured from the initial slope of the curves has a value of $34\frac{1}{2}°$ for the plastic clay and $35\frac{1}{2}°$ for the stable clay; P is the applied normal load. The apparent shear strengths of beds of aggregates of the two very different clays are almost equal.

(ii) At certain normal loads (450 g./cm.^{2} for the plastic clay and there is some evidence of it coming in at 950 g./cm.^{2} for the stable clay) the curve departs from the linear relation indicating either a failure of equation (2) or that the applied normal load is not operating fully on the soil but is being carried to some extent by the soil water. Later evidence supports the second contention, namely that due to the lowered permeability at this degree of compression, the water does not escape fast enough and a positive hydraulic pressure is built up in the soil water. Thus for normal loads greater than 450 g./cm.^{2} for the plastic clay in this machine we are not dealing with an equilibrium process but one that is dependent on the permeability of the compressing soil. The final voids ratio will not be the ultimate voids ratio for the applied load but for the applied load less that carried by the water. This behaviour in a drained test where the water temporarily carries a considerable part of the load and gives the impression of a low shear strength should be obvious in hand testing.

(*b*) *Compression of saturated soil*

In Fig. 4 the ultimate voids ratio for the two soils has been plotted against the logarithm of the applied load P for the saturated condition. Also for both soils the curve for consolidation under a normal load with no applied shear force is given by the broken line. The curves fit the straight-line relation used in soil mechanics work:

$$e = A \log P - C \qquad (3)$$

where C is the voids ratio for unit load P, and A, often called the compression index, is the rate of change of voids ratio with change in log P.

For the plastic clay, where low conductivity prevents an equilibrium voids ratio being reached during shear tests with loads greater than 450 g./cm.^{2}, a correction for that part of the load carried by the soil water has been obtained from the shear strength curve to give an 'effective load' value. The corrected values appear to give a closer fit to the straight-line relation. They also show how the deviation from equilibrium would increase with higher loads.

The beds of aggregates also differ from the ideal clay systems in that the slope of the normal consolidation line is not the same as that of the ultimate voids ratio line. Roscoe has shown that for an ideal clay, regardless of the normal load used, the change in water content between normal consolidation and shearing to failure is a constant. This would require the two lines to be parallel. This deviation from the ideal in the case of aggregates might be due to the gross change in structure which occurs in the artificially packed beds when they are sheared. Alternatively, as we shall see later from the behaviour of a rheological model, the same effect would be obtained where a fraction of the aggregates still persists

at the ultimate condition and the UVR line is then determined in part by aggregate strength.

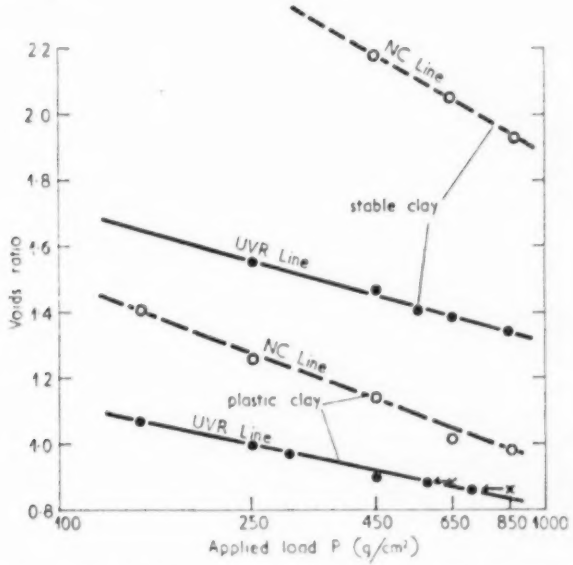

FIG. 4. Normal consolidation and ultimate voids ratio curves for saturated plastic and stable clays. The arrows show corrections made for load carried by soil water.

(*a*) *Unsaturated soil: shear strength*

In Fig. 3 the maximum shear strength of the two soils has been plotted as before against the applied normal load for different degrees of unsaturation. The water content is given as the ratio of the volume of water to the real volume of solids; this identifies the value of the water content with the value of the voids ratio when the soil is compressed to saturation. The general tendency is for the value of the maximum shear strength to be close to the applied load regardless of the soil type or the water content, i.e. to a first approximation, the unsaturated shear strength, S_u is given by

$$S_u = P \tan \phi_u \qquad (4)$$

where ϕ_u, the angle of apparent internal friction for the unsaturated soil, is equal to 45°. A similar result is reported for loose clay soil by Nichols (1932) using an entirely different test machine. He gives a value of tan ϕ_u equal to 1·06 for a loose clay soil. The corresponding values for the two present soils are 1·03 and 1·06 for the plastic and the stable clay respectively.

Deviations from equation (4) occur as might be expected when loads are used which for saturated conditions give ultimate voids ratios

approaching the water content values, i.e. when the load is high enough to compress the soil to saturation. This is seen in the case of curve *OC* for the plastic clay at a water content of 0·86. For loads less than 450 g./cm.^{2} the shear strength is given by equation (4) above. For higher loads the soil is compressed to saturation and the shear strength curve would be expected to follow that for the saturated soil. For the normal load which is just high enough to saturate the soil but not high enough to require excess water to be expressed and so makes no demands on the low permeability (point (*c*)), the shear strength is given by equation (2) on the extrapolated section of the line *OA*. This result supports the earlier assumption that low permeability has caused the deviation, *AB*, from equation (2) for the saturated condition.

(*b*) *Soil water suction and strength*

The shear strength of the unsaturated soil may be explained on the basis of the strength of the saturated soil and the effective load, as determined by the suction in the pore water, and the air-filled porosity. Childs (1955) has shown that suction in a saturated sand has the effect of an equivalent isotropic loading which gives the soil a potential resistance to shear forces equal to the suction load times the coefficient of friction. This is directly additional to shear strength contributed by the applied mechanical load. Thus, taking the total load U, where $U = P+s$, and s is the soil-water suction, in g./cm.^{2}, in the place of the applied load P, we get

$$S = (P+s)\tan\phi_s \qquad (5)$$

which gives the shear strength for the saturated fraction of the soil. This expression implies that the air-filled voids of the soil are on the average carrying a proportional share of the applied load.

To obtain the apparent shear strength S_u, i.e. that measured per unit area of unsaturated soil, a correction is made for the area of contact across any plane in the soil by applying the factor $1-E$, where E is the ratio of the volume of air-filled voids to the total volume.

$$S_u = (P+s)\tan\phi_s(1-E). \qquad (6)$$

Values for the shear strength calculated from equation (6) have been plotted against the experimental values in Fig. 5.

Deviation from the relation occurs to some extent as one might expect at low loads and high voids ratios where the estimate of area of contact $(1-E)$ would be considerably in error. At low loads points of contact rather than areas of contact carry the load, and a better estimate would be obtained from a geometrical treatment as that used by Donald (1956) for unsaturated sands. Furthermore the implication in equation (5) that the air-filled voids are carrying pressures above atmospheric requires explanation in view of Hilf's contention (1956) that at equilibrium the air-space in compressed cohesive soil is in the form of interconnected voids at a pressure equal to the surrounding atmospheric pressure. Generally though the observed values are within ± 5 per cent. of the

calculated values, a deviation of comparatively small magnitude, and it may be concluded that the higher shear strength of the unsaturated soil can be accounted for on the basis of the extra hydraulic loading caused by the suction in the soil water.

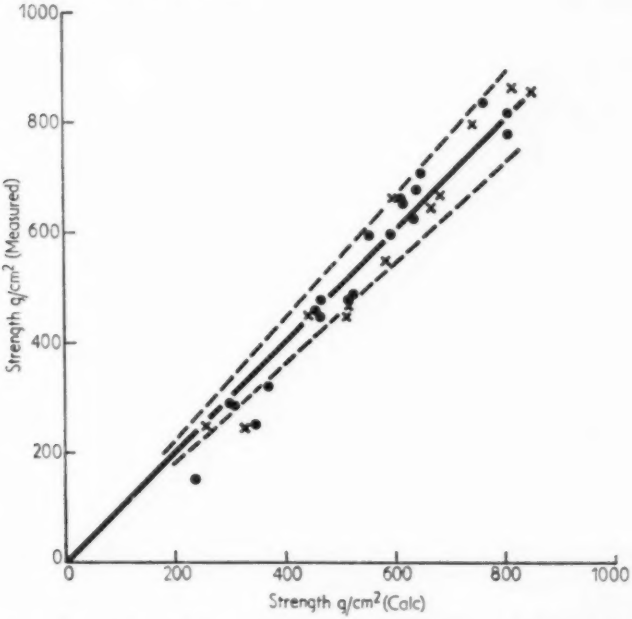

FIG. 5. Comparison of the measured strength of unsaturated clays, plastic (dots) and stable (crosses), with that calculated from equation (6). The broken lines show 5 per cent. deviation limits.

In Fig. 6 the equilibrium water suction in the straining soil has been plotted against water content. Suction is given as centimetres of water plotted on a logarithmic scale, and the figure gives essentially a pF versus water-content relation (Schofield, 1935) as used by Croney and Coleman (1954). Suction versus water-content curves for the undisturbed aggregates are also given. These were obtained by the usual pressure-plate method for both the wetting up and the drying cycles to give a section of the hysteresis loop.

The equilibrium suction for the straining condition bears a relation to the wetting and drying curves for the undisturbed aggregates similar to that described by Croney and Coleman for the disturbed slurried soil. For the unsaturated soil it will be seen that the suction is not greatly affected by the magnitude of the applied load. This is not entirely consistent with the assumptions involving the applied load distribution in equation (6) nor the CVR concept for saturated clay but the explanation is not at present apparent. In the unsaturated case and where aggregates

are only partly broken down one would expect a modification of the equilibrium suction in the straining fraction of the aggregates caused by movement of water into or away from the unstrained fraction. This would have the effect that the mean water content throughout the whole sample might not truly represent conditions in the straining region.

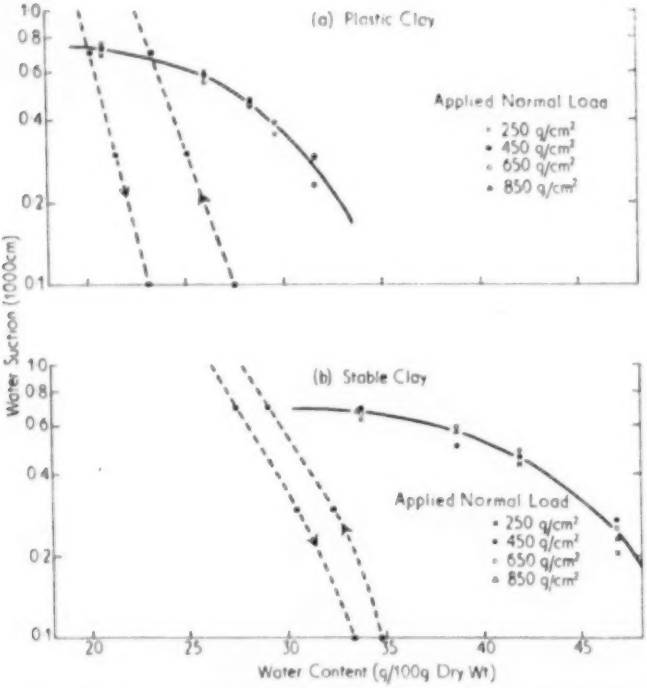

FIG. 6. Ultimate suction developed in soil water on straining an unsaturated bed of aggregates at given soil-water content under different applied loads. The broken lines are pF versus water-content curves for the undisturbed aggregates for both wetting up and drying conditions.

It is probable that the observations made by McMurdie and Day (1958) on water movement occurring during load changes can be explained along these lines.

Another feature of interest in the results is that the suction curves are asymptotic to a value of suction equivalent to about 800 cm. of water. This may be explained on the basis that suctions greater than this are not measurable by means of tensiometers, or, as suggested by Bolt and Miller (1958), by the fact that negative pressures greater than 850 cm. of water are not likely to occur in soils. The pF values greater than the equivalent of one atmosphere suction obtained by Croney and Coleman do not conflict with the above maximum value for suction of about

800 cm. of water, since in this range their values were obtained by a combined suction-plate and pressure-membrane apparatus.

(*c*) *Compression of unsaturated soil*

The equilibrium voids ratio for normal compression and for compression with shear to failure has been plotted against the logarithm of the applied load for both soils in Fig. 7. The ultimate voids ratio line for the

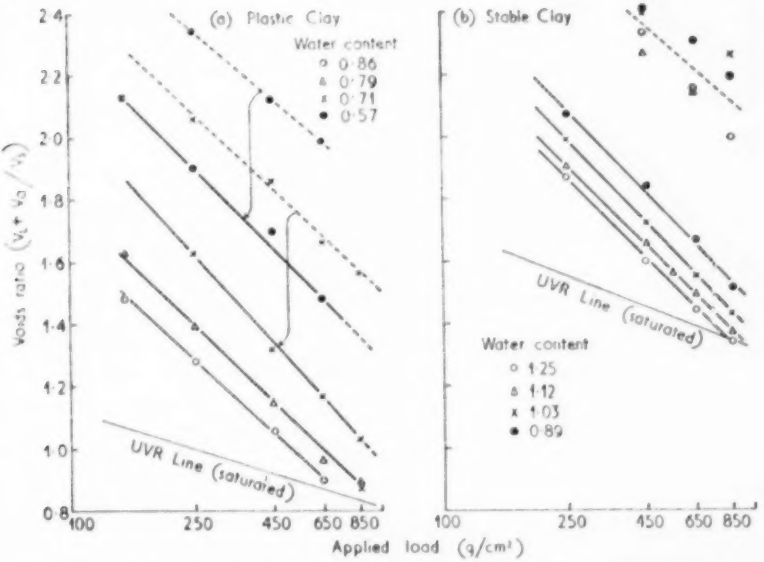

FIG. 7. Normal compression curves for unsaturated beds of aggregates of plastic and stable clays (broken lines) and ultimate voids ratio lines (solid lines) at different soil-water contents.

saturated soil from Fig. 4 is also given. As in the case of the saturated soil the relation may be expressed by equation (3), but with different values for the constants A and C, where C is the voids ratio at unit pressure and A is the slope of the line. It will be noted that the compression index A is reasonably constant for both normal compression and for compression with shear. The value of A is an index of the work used in normal compression. Likewise in the case of the ultimate voids ratio curve, i.e. compression with shear, the slope of the curve is related to the work used in normal compression. Since this work is concerned in part with overcoming resistance to shear forces in the bed (Doner, 1936) the constancy of the A values for the unsaturated tests on both soils supports the finding that the coefficient of shear strength is constant for these conditions. Plots of compression test data from Soehne (1958) and also Nichols (1932) on unsaturated soil also give straight-line relations with

constant values of A over a wide water-content range when plotted in this e versus log P form.

As might be expected the curves also follow the course of increasing to saturation by a fairly abrupt change in slope as the soil goes from the unsaturated to the saturated state. Beyond this point the curve takes on the A value for the saturated soil. Except in the case of the plastic clay at the water content 0·86, the change of slope occurs before the sample is saturated with water. This is shown by the intersection of the saturated curve with the extrapolated unsaturated curve not occurring at the voids ratio equal to the value of the water content. It may be explained on the assumption that air is entrapped in the compressing sample, the amount of air becoming entrapped increasing in soils with initially higher air contents.

For the unsaturated soil a further effect of water content on strength is shown by the range in the value of the constant C, which is the voids ratio at unit strength. To avoid extrapolating the curves of Fig. 7 to unit load we may consider the voids ratio in equilibrium with the applied load of 450 g./cm.^{2}. This value varies from 1·65 to 1·15 for the plastic clay as the water content is increased from 0·57 to 0·86, and for the stable clay from 1·82 to 1·61 as the water content is increased from 0·89 to 1·25. Much of this difference is associated with the water-holding characteristics of the soil material as measured by the Atterberg limits, in particular the lower plastic limit. The voids ratio at 450 g./cm.^{2} for the saturated tests are (from Fig. 7) 0·92 and 1·45 respectively. These values are the lower limits for the voids ratio at this load for the unsaturated soils as the water content is increased to saturation. When they are expressed relative to the lower plastic limit values, i.e. 0·92/0·66 and 1·45/1·12, or 1·39 and 1·30 respectively, much of the difference between the two soils in the spread of the compression curves with water content is explained.

For the two clays, when unsaturated, straining at the lower plastic limit induces suction values between 450 and 650 cm. It would be useful as a simple measure of overconsolidation if a relation between suction and the water content at the lower plastic limit were found for all soils.

A rheological model

The role of water in determining soil strength can be demonstrated by means of rheological models. Numerous workers have shown the pseudo-elastic build-up in strength as saturated clay is strained or compressed. A similar behaviour may be obtained with an arrangement of St. Venant bodies connected in series with springs. The simple St. Venant body possesses friction, and under continuous strain behaves plastically, i.e. it possesses constant shear strength independent of rate of strain. A series of St. Venant bodies demonstrates the work-hardening effect in clays, i.e. the increasing strength with continued strain, while the connexions with springs allows the model to reproduce the condition of set in clays, set being the permanent retention of part of the deformation on unloading (Fig. 8).

If all of the elements are made small in order to represent differentials the arrangement gives a continuous stress–strain curve with a continuous

first derivative. The frictional resistance and the compressibility of the springs may be made an appropriate function of compression so that a stress–strain relation is obtained similar to that for a particular clay. If the St. Venant bodies are enclosed in cylinders, and considered as pistons acting on a fluid, the fractional volume contained in the cylinders

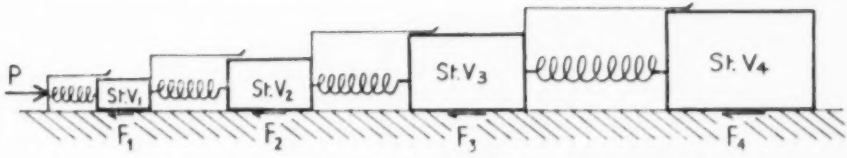

FIG. 8. Simple rheological model consisting of a train of St. Venant (friction) bodies and springs to demonstrate the interplay of frictional resistance and repulsion forces during compression. The friction bodies are enclosed in cylinders containing a fluid to demonstrate the role of the fluid in determining stress–strain behaviour.

is analogous to the voids ratio or the soil-water content. For normal compression without shear it will be seen that after a particular loading, P, the first St. Venant body will begin to slide, the frictional force F_1 being transmitted to the table. The remaining force $(P-F_1)$ will be transmitted by the partly compressed spring to overcome F_2, &c. At some point along the train there will be no movement. This occurs when the sum of the resistances of the friction bodies moved is equal to the applied load. On unloading again to zero load the system expands, but it does not return to its original position. It has acquired frictional set or is overconsolidated. Some of the deformation is retained in the compressed springs, the amount that is retained being determined by the threshold force required to slide the particular bodies outwards again against their frictional force. On reloading and allowing free movement of fluid a typical hysteresis loop will be obtained. The compression curve so obtained, with the unloading and reloading frictional hysteresis loop, is analogous to the voids ratio versus pressure curves of soil mechanics.

To demonstrate the critical voids ratio concept: if now at any point on the compression curve the frictional force is overcome, for example, by a vibration with energy impulses sufficiently high to overcome potential barriers, or by a pure shear force which does not contribute to the normal compression force, the frictional resistance to compression will be destroyed and the pistons will move to an equilibrium position as the springs take up the load. This position will be determined solely by the balance between P, the applied load, and the repulsive force of the springs. The equilibrium position will possess a fractional volume or 'water content' which is characteristic of the spring system and the load. The process is analogous to the situation in clays when a tangential shear force is applied to a compressed sample. The sample changes from the voids ratio in equilibrium with the applied load on the normal consolidation curve to the critical voids ratio for the same applied load. The analogy suggests that while clays are being strained the load is supported

by an apparent repulsive force between the particles, whereas in normal consolidation the load is also supported by frictional or structural forces. In a similar manner if the model has been compressed and then unloaded so that it is over-compressed due to frictional set, and this set is then destroyed as above, the system will expand to the equilibrium position, which is again determined only by the relation between the applied load and the spring force.

For the above systems free movement of fluid has been allowed into or out of the system so that the 'water content' has determined strength only in so far as it is an index of spring compression. Consider now the situation where free drainage is allowed during compression but the fluid is not allowed to re-enter on unloading. It will be seen that the model will not expand again on removing the applied load but the pistons will be restrained by tension which develops in the fluid. Similarly if fluid is supplied on unloading until the model reaches a position of set, the fluid will be under zero tension. If the supply is now cut off and the set is broken by a shear force as described above there will be a tendency for the model to expand or contract to its equilibrium CVR volume; since volume change has been prevented, a tension or a pressure will develop in the fluid which will change the effective load to that demanded by the CVR conditions. The load will then be balanced by the force in the springs plus the tension in the fluid.

This model describes the behaviour of saturated clay where straining is an equilibrium or ultimate process. In the case of the plastic clay it will be remembered that the progress of consolidation under shear was determined by the rate at which water was able to escape from the soil. The model may be modified to represent this mechanism by restricting the rate at which the fluid can escape from the cylinders. Similarly when the overcompressed model is strained, and set is broken, the rate at which the model expands to the equilibrium condition and so its rate of change of strength is determined by the rate at which fluid enters the system. It appears that volume and strength changes in straining overconsolidated clay may be modified by clay permeability and possibly by the negative pressures which clay water is able to support. Paez, as discussed by Torroja and Paez (1954), has designed a model along similar lines to show how the relation between strength and the permeability of concrete might determine cracking behaviour during shrinking. Such models as these should also be useful for describing compaction under short duration loads met with under animal and machinery traffic in agriculture.

IV. *Conclusions*

1. When a loose soil is compressed and sheared in the saturated condition a maximum resistance to shear develops which is linearly proportional to the normal load. This agrees with Hvorslev's equation for shear strength for the special case of consolidation of a slurried clay under normal load. In this case both the cohesion and friction terms of strength are proportional to the applied compression load.

2. There is a unique load–water content–strength relation for strain-

ing saturated clay. In structured clay or in clay that is not straining, owing to the phenomena of work-hardening, set, and hysteresis, compression energy may be either lost or stored in structural bonds, so that no unique water content exists for a particular equilibrium load. As the aggregates strain, the suction adjusts or the water content changes, if possible, towards the CVR condition. In unsaturated soils there is the same tendency for the suction to adjust under the applied load to the equilibrium CVR condition in the region of the aggregate that is straining. Water tends to move to or from this region so that a new balance is reached between the water content and load.

3. The suction in the soil water acts as an added load over the internal area of contact and so increases the potential of the soil to resist strain. The soil compresses under the total effective load to the point where the angle of apparent internal friction is approximately 45° irrespective of the soil type or the water content over the wet range. The unsaturated shear strength is given by:

$$S_u = (P + s)\tan\phi_s(1 - E)$$

where P is the applied load, s the suction in the soil water, $\tan\phi_s$ the coefficient of friction of the saturated soil, and E is the fractional air-filled porosity. S_u, P, and s are given in the same units.

As the soil compresses to saturation the suction becomes zero, $(1 - E)$ approaches unity, and the shear strength is described by the shear strength equation for the saturated soil.

4. For both the saturated and unsaturated state agricultural soil compresses under normal load to a density which appears to be a function of aggregate strength and the initial state of the bed. When a shear force is subsequently applied, the soil compresses further to what has been called the 'ultimate voids ratio', after which there is only negligible change. No proof is offered that the ultimate voids ratio is a final equilibrium value as is the critical voids ratio for ideal clay. There is evidence that it is determined by the water-holding properties of the soil material and by aggregate strength.

5. The rate at which the ultimate voids ratio is approached in unsaturated soil at constant shear is determined by aggregate strength. In saturated soil, above a critical load, poor water conductivity rather than aggregate strength can resist consolidation. This results in the soil water carrying part of the normal load thus causing the soil to exhibit an apparently low shear strength. This relation between strength and impermeability, both of which resist compaction, will be important in determining the amount of permanent strain, when the duration of loading varies.

6. Changes in shear strength are reflected in compression tests on loose soil. The compression index appears to be a constant in unsaturated compression as shown by the parallel voids ratio versus log load plots. This changes to the compression index for the saturated soil as saturation is approached. Normal compression tests and compression tests with shear to the ultimate condition show large differences in strength between

soils at a particular voids ratio. Owing to the relation between the unsaturated and the saturated behaviour the saturated test offers the simplest method for characterizing the strength of agricultural soil.

7. A rheological model has been used to explain the situation existing in soil under compression without shear and in soil that is being compressed and strained at the same time by a shear force. The model also demonstrates the effect of water content on strength.

Acknowledgements

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REFERENCES

AITCHISON, G. D. 1957. The strength of quasi-saturated and unsaturated soils in relation to the pressure deficiency in the pore water. Proc. IVth Int. Conf. Soil Mech. and Foundation Engng., 135–9.

BODMAN, G. B., and RUBIN, J. 1948. Soil puddling. Proc. Soil Sci. Soc. Amer. **13,** 27–36.

BOLT, G. H., and MILLER, R. D. 1958. Calculations of total and component potentials of water in soil. Trans. Amer. Geophys. Union, **39,** 917–28.

BREWER, R., and BLACKMORE, A. V. 1956. Effects of entrapped air and optically oriented clay on aggregate breakdown and soil consistence. Aust. J. App. Sci. **7,** 59–68.

BUTLER, B. E. 1955. A system for the description of soil consistence and structure in the field. J. Aust. Inst. Agric. Sci. **21,** 239–49.

CASAGRANDE, A. 1938. (Ref. from Roscoe *et al.*, 1958.)

CHILDS, E. C. 1955. The physical aspects of some concepts in soil mechanics. Proc. Nat. Acad. Sci. India, **24A,** 86–92.

CRONEY, D., and COLEMAN, J. D. 1954. Soil structure in relation to soil suction (pF). J. Soil Sci. **5,** 75–85.

DONALD, I. B. 1956. Shear strength measurements in unsaturated non-cohesive soils at controlled negative pore water pressures. 2nd Aust.–N.Z. Conf. Soil Mech. and Foundation Engng.

DONER, R. D. 1936. A theory of arch action in granular medium. Agric. Engng. **17,** 299–304.

GREACEN, E. L. 1957. Mechanical stress and disaggregation. Proc. 2nd Aust. Conf. Soil Sci. **1,** 44.

—— 1959. The strength of cultivated soil. J. Agric. Eng. Res. **4,** 60–61.

HILF, J. W. 1956. An investigation of pore-water pressure in compacted cohesive soils. Tech. Mem. 654. U.S. Dept. Int. Bur. Reclam. Colorado.

HOLMES, J. W. 1955. Water sorption and swelling of clay blocks. J. Soil Sci. **6,** 200–9.

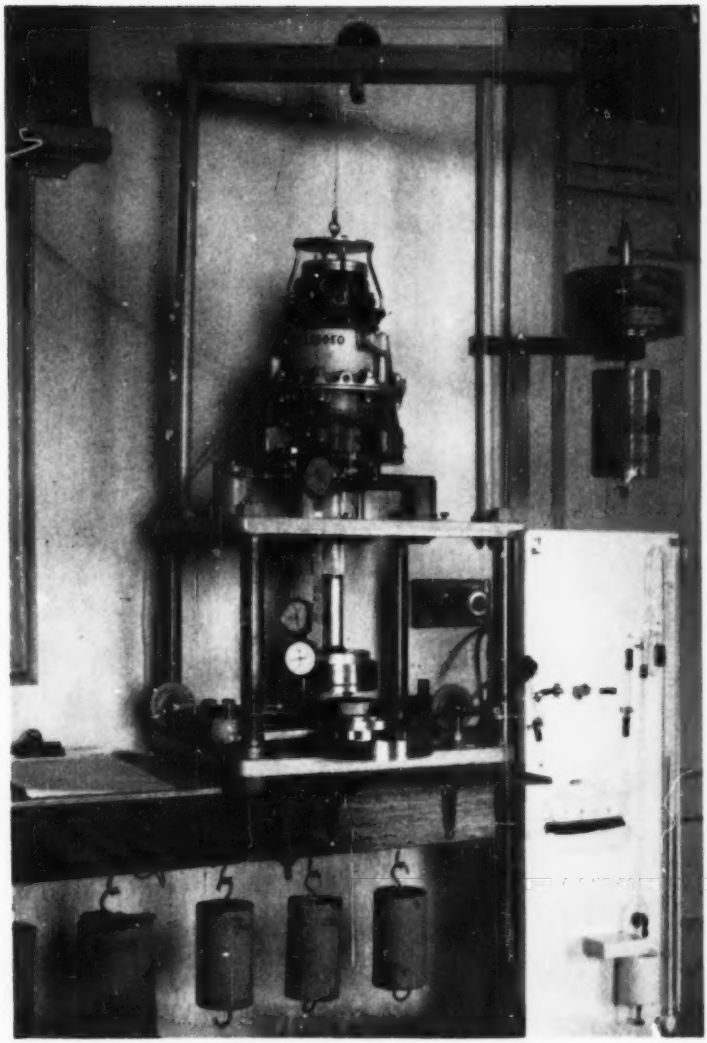
HVORSLEV, M. J. 1937. Über die Festigkeitseigenschaften gestörter bindiger Böden. Ingen. Vidensk. Skr. A. **45,** 159.

—— 1939. Symposium on shear testing of soils. 42nd Ann. Meeting A.S.T.M. 999.

MCMURDIE, J. L., and DAY, P. R. 1958. Compression of soil by isotropic stress. Proc. Soil Sci. Soc. Amer. **22,** 15–18.

MILLER, R. D. 1951. A technique for measuring soil-moisture tensions in rapidly changing systems. Soil Sci. **72,** 291–301.

NICHOLS, M. L. 1932. The dynamic properties of soil. III. Shear values of uncemented soils. Agric. Engng. **13,** 201–4.



The ring-shear machine with null point tensiometer. The outer ring has been removed from the base plate of the cylinder to expose the annulus of soil. Some of the soil has been cut away to show the white tensiometer cup which forms the inner wall of the cylinder.

E. L. GREACEN—PLATE I

ROSCOE, K. H., SCHOFIELD, A. N., and WROTH, C. P. 1958. On the yielding of soils. Géotechnique, **8**, 22–53.

SCHOFIELD, R. K. 1935. The pF of the water in soil. Trans. 3rd Int. Cong. Soil Sci. **2**, 37–48.

SOEHNE, W. 1958. Fundamentals of pressure distribution and soil compaction under tractor tyres. Agric. Engng. **39**, 276–81.

TORROJA, E., and PAEZ, A. 1954. Set Concrete and Reinforced Concrete. Ch. VIII of 'Building Materials', edited by M. Reiner. North Holland Publishing Co., Amsterdam.

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CARBON, NITROGEN, SULPHUR, AND PHOSPHORUS IN SOME SCOTTISH SOILS

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Summary

An examination has been made of carbon, nitrogen, sulphur, and phosphorus relationships in ten surface soils from each of five parent-material groups (calcareous, granite, slate, Old Red Sandstone, basic igneous) in North Scotland. Except that the calcareous soils contain about 40 per cent. less organic carbon, there are no significant differences in the mean contents of total nitrogen and organic carbon. These are highly correlated, but the C:N ratio varies inversely with the base status of the parent material, ranging from 11·3 in the calcareous group to 17·0 for the granite soils.

The total sulphur content is very similar for the four non-calcareous groups, but much higher in the calcareous soils, due to the presence of varying amounts of water-insoluble sulphate, closely related to the calcium carbonate content. Small proportions of this sulphate may be combined with barium and strontium, but most of it is probably present as a co-crystallized impurity in the calcium carbonate. There is a close overall relationship between total sulphur, nitrogen, and organic carbon in the non-calcareous soils and a similar relationship for non-sulphate sulphur in the calcareous group, giving a mean C:N:S ratio of 140:10:1·4 for the five groups. This is similar to ratios from other countries, indicating the general importance of sulphur in soil organic matter.

The organic phosphorus is highest in the basic igneous group and lowest in the calcareous soils, where it comprises 40 per cent. of the total phosphorus compared with 52–61 per cent. in the non-calcareous groups. The proportion of organic phosphorus to the other elements is about 50 per cent. less in the calcareous group, the mean C:N:S:P ratio being 113:10:1·3:1·3, compared with 147:10:1·4:2·5 for the non-calcareous soils. Probably due partly to varying accumulation of inositol phosphates and other resistant forms, the correlations of organic phosphorus with carbon and nitrogen are much lower than for sulphur, and it appears to be a less integral part of the organic matter.

Introduction

SULPHUR and phosphorus occur in soils in both inorganic and organic forms. The amounts and proportions of these two forms vary widely, but in the surface horizons of most well-drained agricultural soils nearly all the sulphur is present in organic forms, while the organic-phosphorus fraction generally comprises 25–66 per cent. of the total phosphorus.

The close relationship between carbon and nitrogen in soil organic matter has been recognized for a long time, but the possible importance of phosphorus and, more particularly, sulphur has only been considered more recently. Many workers have reported positive correlations between organic phosphorus and the amounts of carbon and nitrogen in soils. These results have been summarized by Black and Goring (1953)

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as indicating that the organic matter in mineral soils contains carbon, nitrogen, and phosphorus in an approximate ratio of 110:9:1.

Some of the earlier methods for determining organic phosphorus in soils were subject to errors and did not permit its accurate measurement. Recent investigations, however, by Mehta *et al.* (1954), Saunders and Williams (1955), Kaila and Virtanen (1955), and Legg and Black (1955), have now provided more accurate methods. The development of more suitable methods of estimation (Steinbergs, 1955; Little, 1957) has also facilitated the study of sulphur in soils.

Examinations of both sulphur and phosphorus in soils have recently been made in Australia and New Zealand by Williams and Donald (1957), Walker and Adams (1958), and Williams and Steinbergs (1958). Each reported close relationships between carbon, nitrogen, sulphur, and organic phosphorus, but, whereas the proportions of carbon, nitrogen, and sulphur were similar (C:N:S approximately 135:10:1·3), that of organic phosphorus was more variable. It is now clear that all four elements are associated in the soil organic matter and it is apparent that in addition to nitrogen both sulphur and phosphorus may play important roles in its build-up. For example, Williams and Donald (1957) showed that, in the soils they examined, the amounts of sulphur supplied in fertilizer had controlled the rate of accumulation of organic matter under clover pastures, while Walker and Adams (1958) concluded that the major factor governing the accumulation of organic matter in the soils of the region studied was the phosphorus content of the parent material.

The present paper reports results of an examination of the carbon, nitrogen, sulphur, and phosphorus contents of surface soils representing five parent-material groups in North Scotland.

Soils and Methods

Soils. Ten samples from each of five groups have been examined. Four of the groups represent relatively freely-drained, non-calcareous, acid soils derived from basic igneous, slate, Old Red Sandstone, and granitic glacial tills, and corresponding to the Insch, Foudland, Stonehaven, and Countesswells Associations, respectively (Glentworth, 1954; Macaulay Inst. Ann. Rep., 1955–6); accounts of the phosphorus relationships and other properties of these groups are given by Williams, Scott, and McDonald (1958) and Williams (1959), and with a few exceptions the same samples have been used in the present investigation. The fifth group consists of a collection of calcareous soils, representing mainly littoral deposits of shelly sands forming raised beaches. All the soils are from agricultural land and were sampled to normal plough depth.

Methods. Total carbon was determined by the method of Walkley and Black (1934), which on these soils is known to give good agreement with the more rigorous Van Slyke procedure described by Bremner (1949). Total nitrogen was determined by the Kjeldahl method and total sulphur by the method of Steinbergs (1955). Inorganic sulphate was determined using the same turbidimetric procedure.

Organic phosphorus was determined on all soils by both the ignition

method and the alkali extraction method of Saunders and Williams (1955). For the ignition method 2 N H_2SO_4 was used as extractant. Phosphate in all the extracts was estimated colorimetrically using the reagents of Truog and Meyer (1929) and the technique described by Williams and Stewart (1941). In the determination of total alkali-extracted phosphorus the extract was ignited with magnesium nitrate, and it was found that the molybdenum-blue colour tended to fade somewhat earlier than usual. The onset of fading was related to the phosphate concentration, and above 0·035 mg. P_2O_5 per 100 ml. of final solution it was likely to commence in less than 30 minutes after colour development. At 15 minutes after development the colour was quite stable even for concentrations in excess of 0·10 mg. P_2O_5 per 100 ml., and this time was used for the results in Table 4. The more convenient time of 30 minutes can, however, be used provided the final concentration does not exceed 0·035 mg. P_2O_5 per 100 ml.

Total phosphorus in the calcareous soils was determined by the method of Schricker and Dawson (1939) in the HCl extract of the residue obtained by treating the ignited soil with HF and H_2SO_4. On the non-calcareous soils determinations were also carried out by the fusion method of Muir (1952), and since the two methods gave practically identical results the mean values have been adopted.

Soil pH was determined in 1:2·5 suspension in water by the glass electrode. Estimates of the calcium carbonate contents of the calcareous soils were obtained from the calcium extracted by evaporating the soil to dryness twice with 10 per cent., by vol., acetic acid and then digesting with this reagent; the values include exchangeable calcium but represent mainly calcium carbonate.

Statistical analysis. In addition to the correlation coefficients given in the tables, the standard errors of the mean group properties were determined; these are not included, but statistically significant differences, $p < 0{\cdot}05$, are noted in discussing the results.

Results and Discussion

Carbon and Nitrogen

All but two of the carbon values for the forty non-calcareous soils fall in the range 2·8–7·1 and though the mean, Table 1, tends to be appreciably lower for the Old Red Sandstone soils there are no statistically significant differences between the four groups. The mean carbon content of the calcareous group, however, is significantly lower than those of the basic igneous, slate, and granite groups and on the average it contains almost 40 per cent. less than the non-calcareous soils. The mean nitrogen content also tends to be lowest in the calcareous group, but the range of values is similar for each group, the overall limits being 0·16–0·46 per cent., and there are no statistically significant differences between the means.

The mean C:N ratios, Table 1. follow the sequence: granite > slate > basic igneous > Old Red Sandstone > calcareous, and the following differences are statistically significant: calcareous < all acid groups, granite > Old Red Sandstone and basic igneous, and slate > Old Red

Sandstone. These differences show little relationship with the present pH but they are readily understood on the basis that the C:N ratio indicates the degree of decomposition of the organic matter and varies inversely with the base status of the parent material. The granitic till is the most acidic, followed by the slate; both originally supported Calluna heath and the soils can be classified as cultivated podzols. The marly Old Red Sandstone sediments and the basic igneous till have a higher base status; they originally supported deciduous forest and come into the brown-podzolic and brown earth groups, respectively. Finally, the lowest C:N ratio occurs in the calcareous group which has the highest

TABLE 1

Carbon (Walkley–Black) and Total Nitrogen Contents and Relationships, and pH for Soil Groups

Soil group	*Value*	% C	% N	*Ratio* C:N	*Correlation coefficients* C–N	pH
Granite . .	Mean	4·6	0·27	16·9	0·829*	5·6
	Range	3·1–6·8	0·20–0·41	14·1–20·0		5·2–6·1
Slate . .	Mean	5·0	0·33	14·8	0·886†	5·3
	Range	3·4–7·1	0·26–0·42	11·4–18·2		5·0–6·0
Old Red Sandstone	Mean	3·9	0·29	13·0	0·983†	5·5
	Range	2·0–6·4	0·16–0·44	11·6–14·5		5·1–6·1
Basic Igneous .	Mean	4·8	0·34	14·0	0·932†	5·7
	Range	3·3–6·2	0·24–0·44	11·9–15·7		5·2–6·4
Calcareous .	Mean	2·8	0·24	11·3	0·968†	7·4
	Range	1·6–6·5	0·18–0·46	8·3–14·2		7·0–7·5
All soils . .	..	..	..	..	0·940†	..

*, † Significant at 1 and 0·1 per cent. levels, respectively.

base status. Other factors such as texture, altitude, relative freedom of drainage, and differences in agricultural and manurial practice are doubtless also involved, and contribute to the variations within groups. For example, the lower carbon content and C:N ratio of the Old Red Sandstone group can be attributed to some extent to more frequent cultivation and arable cropping, especially with potatoes.

As would be expected there is a close relationship between carbon and nitrogen, illustrated by the good overall distribution of points in Fig. 1 and the highly significant correlation coefficients in Table 1.

Sulphur

As shown later in Table 3 the mean total sulphur content of the four non-calcareous groups ranges from 0·040 to 0·048 per cent., and there are no statistically significant differences, the range in each group being similar to the overall limits of 0·022–0·069 per cent. The mean total sulphur of the calcareous soils, however, was found to be 0·099 per cent., which is about double the values for the non-calcareous groups and much higher in proportion to the mean contents of carbon, nitrogen, and phosphorus; for example, the mean total sulphur and phosphorus,

Tables 3 and 4, are similar in the calcareous group, whereas in the others the sulphur is only one-third or less of the total phosphorus.

The larger amounts of sulphur in the calcareous soils indicated that they were relatively rich in organic sulphur or in sulphate. The water-soluble sulphate was found to be low, 0·002–0·003 per cent., but extraction with 0·1N HCl removed major amounts (Table 2).

Subtraction of the HCl-soluble sulphate gave N:S ratios much

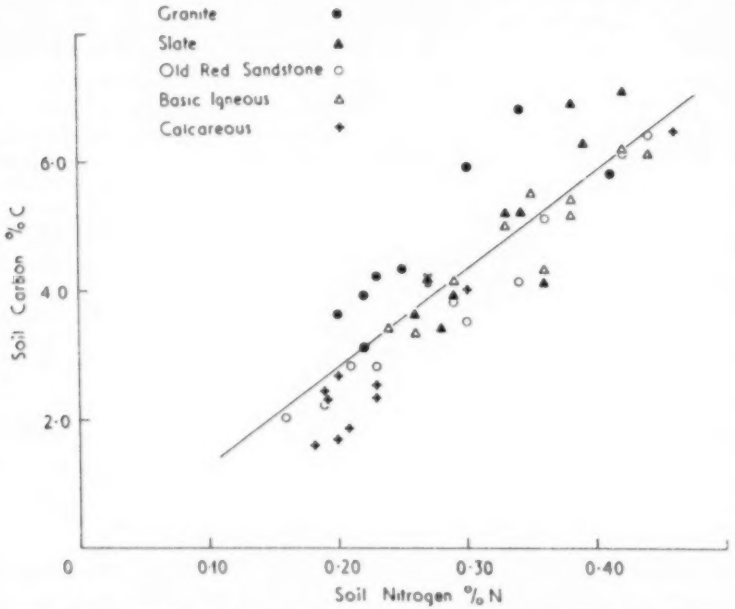

Fig. 1. Relationship between total soil nitrogen and carbon (Walkley–Black).

closer to those for the acid soils although, particularly for the soils high in calcium carbonate, these were still low. Spectrochemical analysis of these soils for total barium and strontium showed that they contained varying amounts of both elements. The amounts of strontium were approximately half those of barium, and in no soil was there sufficient to precipitate sulphate during the acid extraction. The amounts of barium, however, were sufficient to precipitate significant amounts of sulphate.

The low water-solubility of the sulphate in these calcareous soils and the easy release of most of it by HCl extraction suggest that it is associated with the calcium carbonate. As shown in Fig. 2, the total sulphate sulphur (HCl-soluble+sulphate equivalent to barium) is very closely related to the calcium carbonate, the correlation coefficient being 0·972 and significant at the 0·1 per cent. level. This strongly suggests that the sulphate is chemically combined with the calcium carbonate rather than

TABLE 2

Calcium Carbonate, Barium, and Sulphur Contents of Individual Calcareous Soils

Calcium carbonate as % Ca O	*Barium* % Ba	*Total sulphur* % S (*a*)	*Water-soluble sulphate p.p.m.* S	HCl-*soluble sulphate* % S (*b*)	*Sulphate equivalent to barium* % S (*c*)	*Non-sulphate sulphur*• % S (*d*)
19·5	0·050	0·093	24	0·062	0·011	0·020
2·7	0·005	0·053	25	0·010	0·001	0·042
9·4	0·030	0·080	31	0·036	0·007	0·037
29·6	0·100	0·150	22	0·110	0·023	0·017
26·8	0·090	0·179	25	0.131	0·021	0·027
5·3	0·020	0·054	25	0·027	0·005	0·022
1·8	0·005	0·092	25	0·018	0·001	0·073
25·6	0·050	0·159	27	0·122	0·012	0·025
2·2	0·005	0·046	19	0·016	0·001	0·029
12·0	0·030	0·080	23	0·042	0·007	0·031
Mean	..	0·099	25	0·057	0·009	0·033

• $d = a-(b+c)$.

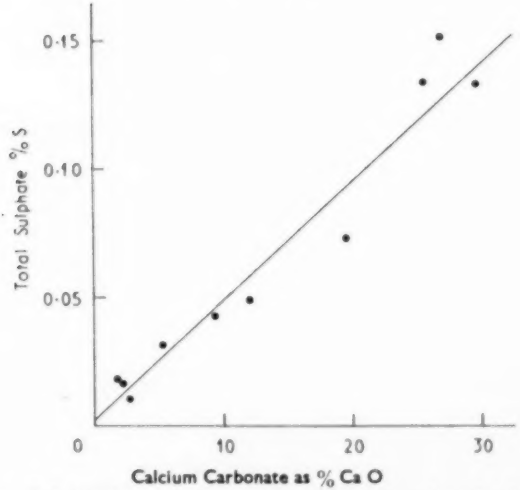

Fig. 2. Relationship between calcium carbonate and total sulphate.

absorbed or occluded by it. The small amounts of barium and strontium present, however, are also closely related to the calcium carbonate, the correlation coefficients being 0·950 and 0·947, respectively, and significant at the 0·1 per cent. level. Some sulphate may, therefore, be present as barium and strontium sulphates, but even if all the barium and strontium were combined with sulphate this would only account for about 20 per cent. of the total sulphate. The relationships cannot be conclusively

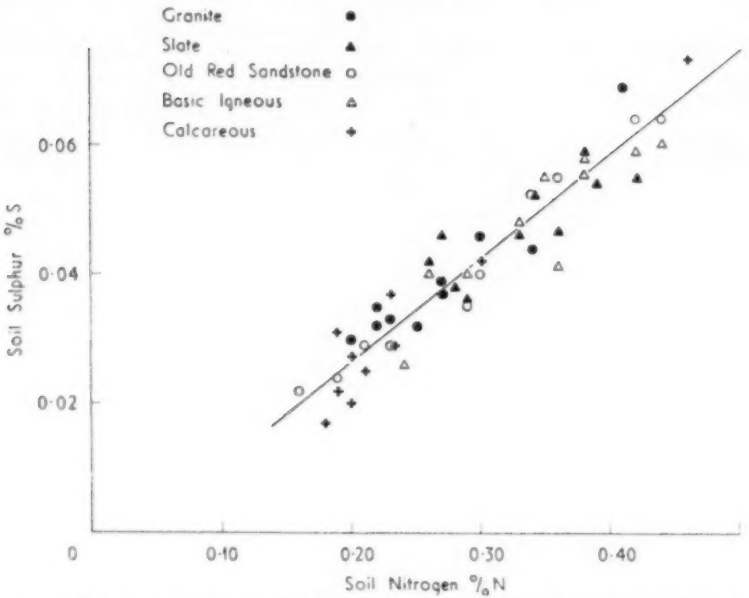

Fig. 3. Relationship between total soil nitrogen and sulphur (total sulphur in the non-calcareous soils, non-sulphate sulphur in the calcareous soils).

TABLE 3

Sulphur Contents and Relationships with Carbon (Walkley–Black) and Total Nitrogen for Soil Groups

Soil group	*Value*	% S*	*Ratios*		*Correlation coefficients*	
			C:S	N:S	C–S	N–S
Granite . .	Mean	0·040	118	6·9	0·690†	0·942§
	Range	0·030–0·069	84–154	5·9–7·8		
Slate . .	Mean	0·047	104	7·0	0·868‡	0·817‡
	Range	0·036–0·060	84–130	6·2–8·0		
Old Red Sandstone	Mean	0·041	94	7·3	0·971§	0·984§
	Range	0·022–0·064	79–111	6·5–8·3		
Basic Igneous .	Mean	0·048	102	7·3	0·926§	0·896§
	Range	0·026–0·060	82–131	6·4–9·2		
Calcareous . .	Mean	0·033	88	7·9	0·898§	0·927§
	Range	0·017–0·073	62–132	6·1–10·6		
All soils . .	..	..	..	..	0·866§	0·938§

* Non-sulphate sulphur for calcareous group, total sulphur for others; total sulphur for calcareous group = 0·099 per cent.

†, ‡, § Significant at 5, 1, and 0·1 per cent. levels, respectively.

resolved from the present results, but it seems highly probable that most of the sulphate is chemically combined with the calcium carbonate and may well be a co-crystallized 'impurity' in the original parent material.

The relationships of carbon and nitrogen with total sulphur for the non-calcareous soils and the corrected, non-sulphate, sulphur of the calcareous soils are given in Table 3, and the overall nitrogen–sulphur relationship is illustrated in Fig. 3.

Sulphur is very highly correlated with both carbon and nitrogen in all groups. The mean N:S ratios, Table 3, fall in the narrow range of 6·9–7·9, and the overall variation for the fifty soils is only 5·9–10·6. The C:S ratio shows relatively wider variations, the overall limits being 62–154, while the group means range from 118 for the granite soils to 94 in the Old Red Sandstone group and 88 in the calcareous group, the granite group being significantly higher than both.

Organic Phosphorus

Organic phosphorus values for all the soils by the two methods described by Saunders and Williams (1955) are given in Table 4.

TABLE 4

Total Organic Phosphorus for Individual Soils by the Ignition Method and by the Alkali Extraction Method, and Group Means for Total and Organic Phosphorus, in mg. P per 100 g. Soil; Mean Values for Percentage Proportions of Organic to Total Phosphorus

Soil group	*Granite*		*Slate*		*Old Red Sandstone*		*Basic Igneous*		*Calcareous*	
Method	*Ignition*	*Extraction*	*Ignition*	*Extraction*	*Ignition*	*Extraction*	*Ignition*	*Extraction*	*Ignition*	*Extraction*
Organic P .	66·8	63·3	93·0	84·7	83·0	69·9	117·4	115·7	40·6	26·2
,,	75·1	73·8	84·3	87·4	60·7	62·4	120·5	120·5	32·3	22·3
,,	68·6	68·6	68·1	62·9	47·6	57·2	58·1	69·4	44·5	40·6
,,	109·1	100·0	82·5	84·7	104·6	96·5	126·2	107·0	17·5	10·5
,,	67·7	69·9	69·0	69·0	87·8	82·1	115·3	96·5	17·0	12·6
,,	58·5	60·7	72·5	69·0	29·2	34·5	134·0	132·7	41·9	28·8
,,	44·1	37·6	89·2	93·0	121·4	112·2	97·8	81·2	50·6	38·9
,,	61·2	61·6	82·5	81·6	82·1	76·8	95·6	72·0	26·7	14·4
,,	75·1	72·9	69·4	68·1	51·5	48·2	92·6	86·0	32·8	30·2
,,	60·6	60·2	81·6	77·7	54·1	50·6	98·2	93·0	29·8	21·0
Mean Organic P . .	68·7	66·8	79·1	77·8	72·2	69·0	105·6	97·4	33·4	24·5
Mean Total P	111		140		121		204		90	
Mean for Organic P as % Total P	61	60	57	56	60	57	52	48	40	26

In general, good agreement was obtained between the two methods on the non-calcareous soils, but, as might be expected, the alkali-extraction method tends to give somewhat lower values, especially for some of the basic igneous soils. For the calcareous soils, the extraction method gives consistently lower values, the mean being nearly 30 per cent. less than by the ignition method. One reason for this could be that ignition increases the solubility in 2 N H_2SO_4 of inorganic phosphorus associated with calcium carbonate, but this seems unlikely because 0·2 N and 2 N H_2SO_4 and 0·2 N, N, and 2 N HCl all gave similar results. As suggested

by Saunders and Williams (1955), the main reason for lower values by the extraction method is almost certainly incomplete extraction, and possibly some hydrolysis, of organic phosphorus by the sodium hydroxide.

During the determination of organic phosphorus by the ignition method, the 2 N H_2SO_4 extracted at least 90 per cent. of the total phosphorus from the ignited soils, the extraction being frequently complete and giving an overall average of 96 per cent.

The generally close agreement between the two completely different methods indicates the suitability of either for estimating organic phosphorus in the non-calcareous soils, and greatly strengthens the validity of the results. Analytically, however, the ignition method is much preferable, and there is little doubt that for all the present soils it is the more reliable method. For comparison with other constituents, therefore, the ignition values have been used for all groups.

As might be expected, both the mean content of organic phosphorus and the proportion of organic to total phosphorus, Table 4, are much lower in the calcareous soils than in the non-calcareous groups. In the latter both the organic and the total phosphorus follow the sequence: basic igneous $\gg$ slate $>$ Old Red Sandstone and granite, the differences between the basic igneous, slate, and granite groups being statistically significant (Williams, 1959), but the mean proportion of organic phosphorus, which varies from 52 to 61 per cent., follows the reverse sequence, the basic igneous group being significantly lower than the granite and Old Red Sandstone. These sequences for the non-calcareous groups are discussed elsewhere (Williams, 1959), but it is relevant to note that there are clear trends for organic phosphorus to increase with acid-oxalate soluble aluminium and phosphate retention capacity; in most instances, however, the organic carbon, which shows no significant differences in the group means, is more closely related to these two properties (Williams, Scott, and McDonald, 1958) than is the organic phosphorus. It is also noteworthy (Williams, 1959) that the lower proportion of organic to total phosphorus in the basic igneous soils may well be largely attributable to the presence of higher proportions of inorganic phosphorus (primary apatite) in the sand fractions; the organic phosphorus in all the non-calcareous soils is present largely in the clays (Williams and Saunders, 1956), and there is no indication that the proportion of organic to total phosphorus is lower in basic igneous clays.

The ratios of carbon, nitrogen, and sulphur to organic phosphorus are given in Table 5, and the group means range as follows: C:P, 47–83; N:P, 3·4–7·7; S:P, 0·47–1·00. In each case the ratio is highest in the calcareous group, where the organic phosphorus is lowest, and lowest in the basic igneous group, where the organic phosphorus is highest. All the differences between these two groups are statistically significant and in most instances they also differ significantly from the slate, Old Red Sandstone, and granite groups, but there are no significant differences between the latter. On the average the calcareous soils contain equal amounts of organic phosphorus and non-sulphate sulphur (S:P = 1·0), and the C:S and N:S ratios, Table 3, are therefore practically the same as the corresponding ratios for organic phosphorus;

TABLE 5

*Relationships of Total Organic Phosphorus with Carbon (Walkley–Black), Total Nitrogen, and Sulphur**

Soil group	*Value*	*Ratios*			*Correlation Coefficients*		
		C:P	N:P	S:P	C–P	N–P	S–P
Granite .	Mean	68	4·2	0·61	0·243	0·251	0·164
	Range	39–91	2·5–6·1	0·36–1·03			
Slate . .	Mean	63	4·2	0·60	0·186	0·250	0·133
	Range	38–85	2·8–4·8	0·43–0·73			
Old Red Sandstone. .	Mean	55	4·3	0·59	0·851‡	0·886§	0·834‡
	Range	40–82	3·4–5·9	0·42–0·91			
Basic Igneous	Mean	47	3·4	0·47	0·215	0·304	0·363
	Range	31–66	2·2–4·5	0·30–0·64			
Calcareous .	Mean	83	7·7	1·00	0·644†	0·321	0·549
	Range	55–129	4·5–11·8	0·49–1·59			
All soils .	..	..	..	..	0·607§	0·639§	0·587§

* Non-sulphate sulphur for calcareous group, total sulphur for others.
†, ‡, § Significant at 5, 1, and 0·1 per cent. levels, respectively.

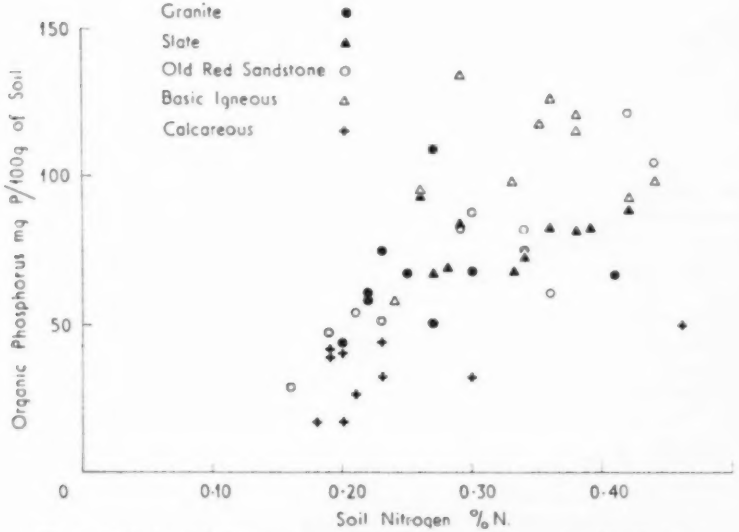

Fig. 4. Relationship between total soil nitrogen and organic phosphorus.

in the acid soils the S:P ratio is only 0·5–0·6, and the C:S and N:S ratios are consequently of the order of twice the corresponding ratios for organic phosphorus.

As shown in Table 5 and Fig. 4, there are significant overall trends for organic phosphorus to increase with carbon, nitrogen, and sulphur.

In the individual groups, only the Old Red Sandstone soils give consistently high correlations, but the calcareous group gives a significant relationship with carbon and a substantial correlation with sulphur. All the other group correlations, however, are very low, and it is clear that all the relationships of organic phosphorus with carbon and nitrogen are much poorer than the corresponding relationships for sulphur, noted earlier in Table 3 and Fig. 3.

General Discussion

The close relationships between the total carbon, nitrogen, and sulphur in the four non-calcareous groups indicate that most of the sulphur in these soils is present in organic forms. As shown by the summary values in Table 6, when the non-sulphate sulphur is taken for

TABLE 6

Mean Ratios of Carbon (Walkley–Black) : Total Nitrogen : Sulphur : Total Organic Phosphorus*

Soil group	*Carbon*	:	*Nitrogen*	:	*Sulphur*	:	*Organic phosphorus*
Granite . . .	169	:	10	:	1·45	:	2·41
Slate	148	:	10	:	1·42	:	2·37
Old Red Sandstone .	130	:	10	:	1·37	:	2·35
Basic Igneous . .	140	:	10	:	1·37	:	2·97
Calcareous . . .	113	:	10	:	1·27	:	1·32
All soils . . .	140	:	10	:	1·38	:	2·28

* Non-sulphate sulphur for calcareous group; total sulphur for others.

the calcareous soils all five groups give similar C:N:S ratios, indicating a similar average composition of the organic matter with respect to these three elements.

The average ratio over all soils, C:N:S = 140:10:1·4, is similar to ratios found elsewhere, by Williams and Donald (1957), 155:10:1·4, Walker and Adams (1958), 120:10:1·3, and Williams and Steinbergs (1958), 150:10:1·3, and to the corresponding values calculated from the data of Evans and Rost (1945,) 122:10:1·5. The similarity of these ratios reported from widely separated parts of the world supports the conclusion that sulphur is an important constituent of soil organic matter, generally.

As already discussed, the sulphate in the calcareous soils may be present to small extents as barium and strontium sulphates, but it is highly probable that most of it is chemically combined with the calcium carbonate and may well be a co-crystallized impurity in the original parent material.

Although the C:P and N:P ratios are significantly lower in the basic igneous group, it may be said that within wider limits the organic matter in the four non-calcareous groups has a similar average composition with respect to phosphorus as well as sulphur; the mean C:N:P ratios are 147:10:2·5 and similar to the values of 120:10:2·7 reported by Walker

and Adams (1958) for New Zealand soils. The proportions of organic phosphorus in the calcareous group, however, are about 50 per cent. smaller, the corresponding ratios being 113:10:1·3, and similar to the average values of 110:9:1 (122:10:1·1) quoted by Black and Goring (1953).

The above ratios indicate that the proportion of organic phosphorus to organic matter is more variable than is the case for sulphur. In the present soils, this is conclusively shown by the fact that although there are significant overall trends for organic phosphorus to increase with carbon and nitrogen, the correlations are much lower than for sulphur and only three of the ten group coefficients are significant, the other seven being of the order of only 0·13–0·32, Table 5. For reasons given earlier, it is most unlikely that this is due to any appreciable extent to errors in the organic phosphorus estimations. The relationships are, of course, subject to possible differential influences of numerous agricultural, physical, chemical, and microbiological factors, including the amounts and composition of organic residues, the balance between organic and inorganic phosphorus, and soil properties and conditions such as pH, soluble aluminium, phosphate retention capacity, temperature, drainage, and aeration. The variations in C:P ratios within the non-calcareous groups, for example, may hinge partly on drainage; all the soils are relatively freely-drained, but there are appreciable differences and it is known that the C:P ratio is markedly lower under poorer drainage conditions, due mainly to much lower organic phosphorus content (Williams and Saunders, 1956). As pointed out by Williams and Steinbergs (1958), a more specific factor to be considered is the occurrence of inositol phosphates. No information is available for the calcareous soils, but the results of Anderson (1956) indicate that about 20–40 per cent. of the organic phosphorus in the acid soils may be present in this form, mainly the hexaphosphate. These compounds contain no nitrogen and sulphur and the C:P ratio of the hexaphosphate is only about 0·4. It is quite likely, therefore, that one factor limiting the correlations between phosphorus and other constituents of the organic matter in the present soils is varying accumulation of inositol phosphates and other resistant organic phosphorus compounds. More detailed information on the nature and distribution of such compounds in the different soils and on their relationships with soil properties is necessary to clarify this aspect.

To sum up, it is clear that carbon, nitrogen, and sulphur are closely associated in the soil organic matter, and it seems possible that the proportions may be defined within moderately narrow limits by microbial decomposition. The relationships with organic phosphorus, however, are more complex and it seems to be a less integral part of the bulk organic matter, probably due partly to varying and more independent accumulation of resistant organic phosphorus compounds such as inositol phosphates.

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REFERENCES

ANDERSON, G. 1956. J. Sci. Food and Agric. **7**, 437.
BLACK, C. A., and GORING, C. A. I. 1953. Soil and Fertilizer Phosphorus, p. 123. Academic Press, New York.
BREMNER, J. M. 1949. Analyst, **74**, 492.
EVANS, C. A., and ROST, C. O. 1945. Soil Sci. **59**, 125.
GLENTWORTH, R. 1954. The Soils of the Country round Banff, Huntly and Turriff (Sheets 86 and 89). Mem. Soil Survey of Great Britain: Scotland. H.M.S.O.
KAILA, A., and VIRTANEN, O. 1955. Maataloust Aikak. **27**, 104.
LEGG, J. O., and BLACK, C. A. 1955. Soil Sci. Soc. Amer. Proc. **19**, 139.
LITTLE, R. C. 1957. J. Sci. Food and Agric. **8**, 271.
MACAULAY INST. SOIL RES. 1955–6. Ann. Rep., Appendix.
MEHTA, N. C., LEGG, J. O., GORING, C. A. I., and BLACK, C. A. 1954. Soil Sci. Soc. Amer. Proc. **18**, 443.
MUIR, J. W. 1952. Analyst, **77**, 213.
SAUNDERS, W. M. H., and WILLIAMS, E. G. 1955. J. Soil Sci. **6**, 254.
SCHRICKER, J. A., and DAWSON, P. R. 1939. J.A.O.A.C. **22**, 167.
STEINBERGS, A. 1955. Analyst, **80**, 457.
TRUOG, E., and MEYER, A. H. 1929. Ind. Eng. Chem. Anal. Ed. **1**, 136.
WALKER, T. W., and ADAMS, A. F. R. 1958. Soil Sci. **85**, 307.
WALKLEY, A., and BLACK, I. A. 1934. Ibid. **37**, 29.
WILLIAMS, C. H., and DONALD, C. M. 1957. Aust. J. Agric. Res. **8**, 179.
—— and STEINBERGS, A. 1958. Ibid. **9**, 483.
WILLIAMS, E. G., and STEWART, A. B. 1941. J. Soc. Chem. Ind. Trans. **60**, 291.
—— and SAUNDERS, W. M. H. 1956. J. Soil Sci. **7**, 90.
—— SCOTT, N. M., and MCDONALD, M. J. 1958. J. Sci. Food and Agric. **9**, 551.
—— 1959. Agrochimica, **3**, 279.

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TRACE-ELEMENT DISTRIBUTION IN SOIL PROFILES

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Summary

The contents of total and extractable trace elements present in Scottish soil profiles are primarily related to the geological parent material from which the soils are derived. Little or no effect within the profile attributable to pedological factors has been observed in the total contents. The most marked effect on the contents of extractable trace elements, notably Co, Ni, Cu, Mn, Mo, Zn, and Pb, is their increased mobilization in conditions of restricted drainage. Very high extractable contents occur in gleyed horizons of very poorly drained soils. No marked accumulation of trace elements has been observed in the iron pan or illuvial horizons of podzolized profiles. Higher contents of acetic-acid-extractable Al occur in soils with unrestricted drainage, the amounts present being of the same order as the exchangeable-Ca contents.

Introduction

THE determination of the total and extractable contents of metallic trace elements in over 100 Scottish soil profiles developed on contrasting parent materials has given sufficient information to indicate the general principles governing their distribution in the soils of Scotland. These soils are of diverse geological origin and pedological character, and it is possible to consider only a few characteristic types which serve to illustrate the principles involved. The purpose of this communication is to report the levels of total and extractable trace elements normally found in Scottish soils: detailed discussion of the factors involved in their distribution must await further investigation.

The total contents of the trace elements in any soil are directly related to the nature of the rocks from which it was derived; from this point of view, the geological parent material is of crucial importance in soil classification, and this supports the use by the Soil Survey of Scotland of the soil association based on this characteristic. Some of the complex geochemical principles involved have already been summarized (Mitchell, 1955*a*) and need not be discussed here. It is also unnecessary to review the early literature concerning the occurrence of trace elements in soils, as a comprehensive bibliography is available (Swaine, 1955). More recent information has been reported by Gammon, Henderson, Carrigan, *et al.* (1953), Butler (1954), Wright, Levick, and Atkinson (1955), Lounamaa (1956), Walsh, Ryan, and Fleming (1956), McKenzie (1956, 1957), Tiller (1957), Vinogradov (1957), and Kovda and Vasilyevskaya (1958). The spectrochemical methods which were employed for the analytical determinations have been fully described elsewhere (Mitchell, 1948, 1955*b*; Mitchell and Scott, 1957).

Total Contents of Trace Elements

Eight profiles have been selected to illustrate the range of occurrence of trace elements in Scottish mineral soils, and their total contents are

recorded in Table 1, A-H. Pedological descriptions of the soil associations and series will be found in the Annual Reports of the Macaulay Institute and in recent or forthcoming Memoirs of the Soil Survey of Great Britain (Scotland). The parent rocks range from ultrabasic to acidic igneous and from arenaceous to argillaceous sediments. The soils have been developed on glacial tills which have been transported longer or shorter distances from the parent rocks. There must inevitably have been some size-sorting and admixture of extraneous material in the course of the formation of the boulder clays, particularly in areas where the geology is complex. The profiles considered here have all developed, as far as can be ascertained, on reasonably uniform parent material, but nevertheless this aspect must be kept in mind in considering any variation in content which may be observed. The total (but not the extractable) contents were determined by semi-quantitative spectrographic assessment, with a precision of the order of 30–50 per cent., and smaller variations must be disregarded. This is less disadvantageous than might appear at first sight, in view of the effects of the factors just mentioned and because of the great variations in trace-element content, sometimes as much as 100- or even 1,000-fold, which can occur from profile to profile. The diagnosis of the less drastic pedological processes by total analysis is ruled out, but these are better studied by extraction techniques.

The eight profiles have been selected to include some of the more divergent types encountered in Scotland, and can be taken to cover the normal range of occurrence of most trace elements. Profiles with a surface horizon designated S are currently cultivated, others are from areas in permanent grass or open moorland. No forest soils are included in this study.

(a) Geochemical distribution

The first point to be emphasized is that the total contents of trace elements in the soil parent materials, as indicated by the results for the lower horizons, are related to their geological origin. Profiles A-D (Table 1) have been developed on tills derived from igneous rocks of increasing SiO_2 content, passing from a serpentinized early-crystallizing ultrabasic olivine rock (A) through basic gabbro (B) to intermediate andesite (C) and SiO_2-rich granite (D). In this series the distribution follows the principles laid down by Goldschmidt (1937) and observed by Wager and Mitchell (1951) and Nockolds and Mitchell (1948) for rocks and their constituent minerals. The contents of the elements Cr, Ni, and Co fall steadily from the basic to the acidic parent materials, while the opposite holds for Li and Rb. The high content of Zr in the ultrabasic soil is less readily explained. The highest contents of Mn, Cu, V, Sc, and one or two other elements occur in soils derived from intermediate rocks, in accordance with expectation. The marked differences in the Ni:Co ratios also accord with those found in the above publications, this ratio being lowest in the andesitic soils, in which the Co content can exceed that of Ni. Of the less abundant trace elements, Be is observed only in the acidic and Mo in the ultrabasic soils.

In the second group of four profiles (Table 1, E-H) it is seen that the granitic-gneiss soil (E) does not resemble the previously discussed granite soil (D) in its suite of trace elements, being considerably higher in Cr, Co, Ni, Cu, V, Ba, and Sr, and corresponding more closely to the soils derived from quartz-mica-schist (F) and silurian slate (G), both of which are definitely of sedimentary origin. This is a point which requires further geological investigation, but in view of the long controversy regarding the origin of granites, it seems that detailed study of their trace-element contents might be valuable. The difference in Co and Ni contents between the two granitic soils is, in our experience, greater than that normally found between soils derived from igneous rocks of like geological origin.

There is a very marked difference between the trace-element contents of the soils from the argillaceous and arenaceous sediments, the sandstone (H) having generally much lower contents than the schist and slate. The argillaceous soils have, in general, contents near the mean values of those of igneous origin already considered. This is not unexpected, as their parent rocks must have been derived in the first instance from igneous rocks. An obvious exception is Pb, which appears to be more abundant in rocks of sedimentary origin, an effect attributed by Wedepohl (1956) to volcanic exhalation. The findings suggested by the results quoted are fully substantiated by the further results available, but for which it is impossible to find space.

The practical significance of the systematic distribution of the trace elements in soils of different geological origin arises from the importance of trace elements in plant and animal nutrition. Absolute deficiencies of such elements as Cu and Co are liable to occur in sandstones and certain granites, while excesses of Ni are most likely to be associated with ultrabasic rocks. Although the argillaceous sediments reported here are relatively low in Mo, contents up to 20 p.p.m. occur in some Scottish soils derived from such sedimentary or metamorphic rocks, and it is on soils from argillaceous parent materials that Mo poisoning of stock may occur. Many other factors are involved, but the ability to assess the probable total content of any trace element in a soil from a knowledge of the geological nature of its parent material is of considerable value. The explanation of the causes of the geochemical distribution, involving such factors as ionic radius and ionic potential, is scarcely a pedological problem and therefore outside this discussion. The treatises by Goldschmidt (1954), Mason (1952), or Rankama and Sahama (1950) provide the necessary background information.

(*b*) *Pedological distribution*

In this section the effects of pedological and biological factors in producing variations in the total contents of trace elements within the profile will be considered. Examination of Table 1 shows that in general, taking into account the analytical limitation already mentioned, no great variation in content from horizon to horizon is obvious. In fact, for most elements, little significant change in the total content that can be ascribed to pedological factors is apparent. This is not unexpected,

TABLE 1

The Total Content of Trace-elements in Scottish Soil Profiles (expressed as parts per million in air-dry soil)

1A. *Brown podzolic soil, freely drained, on serpentine till, Aberdeenshire. Leslie association, Leslie Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
S	2–7	30·2	10·3	4·2	1,500	<5	40	3,500	7	30	30	10	1,500	1	600	20	60	<10	400	12,000	70	30	>1,000
B_1	8–12	7·4	17·6	6·2	800	<5	200	2,000	15	20	<10	20	3,000	5	5,000	10	30	<10	200	6,000	100	30	1,000
B_1	18–22	5·8	16·1	6·8	1,000	<5	150	2,000	15	20	20	30	5,000	3	3,000	10	60	<10	300	9,000	100	30	1,000
B–C	26–30	5·4	14·4	7·7	1,000	<5	200	3,000	25	20	10	30	2,000	7	3,000	10	70	<10	200	6,000	80	40	1,000
C	38–43	5·6	16·5	7·5	1,000	<5	200	3,000	25	20	15	20	3,000	5	3,000	10	40	<10	200	4,500	80	30	1,000

1B. *Brown podzolic soil with gleyed B and C horizons, imperfectly drained, on olivine gabbro till, Aberdeenshire. Insch association, Glebe Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
S	0–8	14·7	19·5	6·0	2,000	<5	40	300	30	50	<10	30	7,000	<1	70	20	50	15	800	25,000	200	30	70
B_1	12–15	7·1	15·4	5·6	2,000	<5	40	100	30	50	<10	30	7,000	<1	70	10	70	15	800	20,000	200	30	100
B_2 (g)	16–19	5·7	11·2	5·7	2,000	<5	40	200	30	50	<10	30	5,000	<1	70	10	70	15	800	22,500	200	30	100
B_2 (g)	20–24	6·2	17·5	5·9	2,000	<5	40	300	40	50	10	40	7,000	<1	70	10	60	15	800	12,500	300	40	200
C (g)	36–44	3·6	20·8	6·1	2,000	<5	40	300	40	50	<10	40	7,000	<1	70	10	80	15	500	20,000	200	30	100

TABLE 1 (*cont.*)

1C. *Brown forest soil (low base status), freely drained, on andesitic moraine, Renfrewshire. Darleith association, Darleith Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
S	1–7	14·8	20·2	6·0	600	<5	10	80	25	20	30	50	1,000	<1	25	40	50	<10	150	10,000	150	30	250
B_2	10–14	7·8	11·0	6·4	600	<5	20	60	30	20	30	80	1,000	<1	20	10	60	<10	200	12,000	150	30	200
B–C	18–26	7·1	9·1	6·5	600	<5	20	40	20	25	30	80	1,000	<1	20	10	100	<10	200	12,000	200	40	200
C	29–33	5·2	9·4	6·6	800	<5	20	150	20	25	40	60	1,000	1	15	10	60	<10	150	12,000	200	60	200

1D. *Peaty gleyed podzol with iron pan, poorly drained above, freely drained below pan, on granitic till, Kincardineshire. Countesswells association, Charr Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
H	7–9	65·7	..	4·2	250	8	<1	7	3	10	50	20	50	<1	4	50	400	3	100	1,000	15	20	200
A_3	10–14	5·8	6·3	4·4	800	15	<3	25	<5	20	70	80	200	<1	8	15	1,000	<10	100	2,000	25	50	800
A_3	17–21	9·5	11·2	4·6	800	15	<3	30	<5	40	70	80	300	<1	10	20	700	<10	100	3,000	50	30	800
B_1	21	16·0	..	..	800	20	3	50	<5	30	40	150	300	<1	10	20	1,000	<10	150	3,000	80	40	300
B_2	21–25	6·2	12·3	4·9	800	20	3	30	<5	30	70	200	300	<1	15	30	700	<10	100	1,000	50	50	300
B_2–C	31–36	3·4	6·3	4·8	500	25	3	20	<5	40	150	200	500	<1	8	30	1,500	<10	150	1,000	30	30	500
C	40–46	3·1	7·6	4·9	500	30	3	20	<5	30	150	200	500	<1	10	20	1,000	<10	150	2,000	50	100	800

TABLE 1 (*cont.*)

1E. *Podzol, freely drained, on granitic gneiss till, Aberdeenshire. Countesswells association, Countesswells Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
S	0–10	8·9	12·7	5·4	3,000	5	10	200	25	70	200	70	1,000	<1	40	70	500	<10	700	7,000	250	80	800
B_1	12–14	3·5	8·1	5·4	2,000	5	20	150	30	70	100	50	1,000	<1	60	30	500	<10	700	5,000	150	60	800
B_2	16–20	3·3	15·5	5·5	3,000	5	20	150	50	50	150	70	2,000	1	50	30	700	10	800	5,000	150	100	500
B_3	24–30	3·1	17·7	5·3	3,000	5	20	150	50	50	100	50	2,000	<1	80	20	500	10	800	5,000	150	80	1,000
C (g)	37–41	3·3	20·6	5·4	2,000	5	20	200	50	50	100	50	1,000	2	80	20	500	10	800	6,000	150	60	800

1F. *Podzol, freely drained, on quartz mica schist till, Kincardineshire. Strichen association, Strichen Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
S	0–7	10·2	33·2	6·5	1,500	5	25	150	25	40	100	200	3,000	5	80	80	200	10	150	9,000	200	100	>1,000
B_1	13–19	6·3	16·8	5·3	1,500	5	30	150	30	40	100	200	2,000	5	100	50	200	10	150	9,000	200	80	1,000
B_2	24–27	8·0	14·4	5·3	1,500	5	40	150	40	40	100	200	2,000	3	150	30	200	10	100	9,000	200	80	1,000
B_3	32–38	5·1	20·0	5·4	1,500	5	40	150	40	40	100	200	3,000	1	150	30	200	10	100	12,000	200	80	>1,000
C	40–43	4·4	18·5	5·4	2,000	5	30	200	40	50	100	200	2,000	2	70	70	300	<10	100	9,000	150	50	1,000

TABLE 1 (*cont.*)

1G. *Non-calcareous gley, poorly drained, on silurian slate till, Roxburghshire. Ettrick association, Ettrick Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
A_1 g	2–5	15·2	25·8	4·8	700	<5	10	250	5	30	100	60	300	<1	40	40	250	10	50	8,000	200	60	700
A_3 g	5–9	5·2	43·1	5·3	500	<5	20	250	20	30	100	60	500	<1	80	15	200	10	50	8,000	200	40	700
B_1 g	11–14	8·5	46·8	5·2	700	5	30	250	40	25	40	80	500	<1	80	10	200	10	50	8,000	200	40	700
B_2 g	16–20	5·3	46·3	5·6	700	5	25	200	40	25	40	80	800	<1	100	20	200	15	70	8,000	200	60	500
B_2 g	24–30	4·7	49·9	7·3	700	5	20	200	40	25	60	100	600	<1	100	15	200	15	70	8,000	200	60	500
Cg	36–42	7·1	49·8	8·3	700	5	20	200	40	20	60	100	800	<1	80	15	200	20	150	8,000	200	80	500

1H. *Peaty podzol with iron pan, freely drained below pan, on sandstone till, Ayrshire. Largs association, Haupland Series.*

Horizon	*Depth*	% *Loss on ignition*	% *clay*	pH	Ba	Be	Co	Cr	Cu	Ga	La	Li	Mn	Mo	Ni	Pb	Rb	Sc	Sr	Ti	V	Y	Zr
A_2	1–2	10·4	7·8	4·0	800	<5	<3	20	<5	15	60	8	80	<1	8	40	40	<10	40	4,000	60	40	400
B_1	5–14	5·5	13·8	4·4	800	<5	4	30	<5	15	40	8	400	<1	15	10	40	<10	40	4,000	60	40	400
B_2	22–27	1·9	13·7	5·0	1,000	<5	4	25	<5	8	60	8	600	<1	20	10	40	<10	40	3,000	40	40	600
C	35–40	2·1	12·7	5·2	1,000	<5	3	10	<5	8	80	6	600	1	15	10	40	<10	40	1,000	60	40	400

The discontinuous iron pan (B_1) at 2 in. is unfortunately not available.

as a large proportion of the trace-element content is bound up in the crystal lattice of the constituent rock-forming minerals, notably the ferromagnesian silicates and the aluminosilicates. In normal conditions the proportion of such minerals which undergo weathering is relatively small and the amounts of trace elements available for pedological translocation are also small. There are a few exceptions to which attention will be drawn. At this point, however, mention should be made of the possibility of diagnosing pedological size-sorting by trace-element examination. It is known that the smaller size fractions, notably the clay fraction, often contain greater amounts of certain, but not all, trace elements than do the sands, and a knowledge of the content of such elements in the whole soil can be valuable in indicating whether a clay-rich layer has been formed by the transportation of clay from other horizons, or by the increased formation of clay *in situ* by weathering.

The first profile (Table 1A), developed from ultrabasic rock, is somewhat exceptional in that a number of the trace elements have much smaller contents in the surface horizon than lower in the profile. It is those elements occurring in the readily serpentinized olivine crystals of the original rock which show this decrease in the surface horizon, and the explanation for the low contents of Co, Cu, Mn, Mo, and Ni must lie in their being leached after complete weathering of their parent minerals. The opposite holds for Cr and Ti, which are presumably present in less readily weathered minerals. The surface horizon of this soil is much more acid than the lower horizons, and quite high in organic matter. These effects are obvious only in the profile developed on this rather exceptional ultrabasic parent material. In the other profiles, when the mineral matter content, undiluted by organic surface accumulation, is taken into account, there is to be noted, in one or two instances only, a lower content in the surface horizon of Li and Rb, readily leached alkali metals.

Apart from these effects, there are few differences which can be attributed to leaching, even in the well-developed podzols (Tables 1D, 1H). In the granitic profile (1D) the total Fe contents in upper and lower A_2, B_1 (iron pan), and B_2 horizons are respectively 0·24, 1·01, 5·37, and 2·00 per cent. Similar relative variations in the trace elements would readily be observed by the technique employed, but for Ni, for instance, there is no evidence of such podzolic translocation.

The surface accumulation of Pb is the outstanding effect observed in the total trace-element contents of the profiles examined. This is apparent in all the profiles in Table 1. Even greater increases have been observed in other profiles; in fact some quoted here (Table 1E, 1F) are among the least marked which have been encountered. Tenfold increase, calculated on the basis of the air-dry material in the surface horizon, is not uncommon. The effect is greatest in organic-rich uncultivated surface horizons, and is even more pronounced when expressed on a mineral matter or ash basis. One uncultivated profile on granite for which results are available contains 20–30 p.p.m. Pb in the horizons A_2 to C (4 to 42 in.) and 550 p.p.m. Pb in the 1–3 in. A_1 horizon. These soils are generally remote from industrial areas and

from high-density motor traffic; being uncultivated, contamination from tractors is excluded. The obvious explanation would appear to be an accumulation of Pb through plants, much more pronounced than for other elements. Presumably an insoluble complex which holds the Pb in the surface horizon—whether organic or inorganic is not yet established—is being formed on the decay of the plant material. The smaller effect seen in profiles 1E and 1F may be because both are derived from metamorphozed sediments which have previously undergone weathering and possibly incorporate immobilized or unavailable Pb throughout the profile. In this connexion it is interesting to note that the only observed occurrences of Ge in Scottish soils have been in the A_0 horizon of podzols or peaty podzols derived from arenaceous material of Old Red Sandstone or Silurian greywacke origin. The contents found were 2–5 p.p.m. Ge in the dry matter, corresponding to 10–20 p.p.m. on a mineral basis, there being 65–90 per cent. loss on ignition. A concentrating factor similar to that for Pb would appear to be operating.

In contrast to these findings, reports occur in the literature which indicate the leaching of trace elements from surface horizons to an extent readily observed in the total contents. Walsh, Ryan, and Fleming (1956) quote figures showing much higher total Co contents in the B than in the A horizons of podzolized soils in Ireland. Such effects have only been observed in Scotland in soils derived from ultrabasic rocks. A similar effect is suggested by the statistical analysis by McKenzie (1957) of the results for Co, Cu, Ga, V, and Mo in fourteen South Australian red-brown earth profiles, but detailed consideration of the individual profiles (McKenzie, 1956) shows that in nine of the fourteen profiles little or no differentiation with depth is apparent, while in five profiles from one area there is a very low content (Co <2) in the surface horizons (to 12 in. in some cases) with an abrupt rise to over 10 p.p.m. immediately below. It seems that something more fundamental than simple trace-element leaching is involved, in view of the marked textural differences which also occur. Wright, Levick, and Atkinson (1955) have examined the total Zn, Pb, Cu, Co, Mn, and Mo contents of a number of Canadian soils of different groups. They also found a marked accumulation of Pb in the A_0 horizons of podzol and brown podzolic profiles. Copper is stated to be the element most susceptible to leaching, although high Cu is reported in several surface litter horizons. The distribution of Mn is irregular. There are increases in the total Co content in the B horizons of these podzolized soils from Canada.

Extractable Trace-element Contents

Pedological processes can affect the trace-element status of soil horizons in two distinct ways. There may be alterations in the total content, due to translocation or removal, and there may be alterations in the mode of occurrence which may or may not lead to a change in ease of extraction or plant availability. Changes in the relative degree of extraction will be considered in this section. The reagents which have been employed are 2·5 per cent. acetic acid, neutral normal ammonium acetate, and, occasionally, water. The methods of extraction

and determination are described elsewhere (Mitchell, 1948, 1957; Mitchell and Scott, 1957). The quantitative spectrochemical methods employed give a reproducibility of the order of ± 10 per cent. Extractants provide results which help to clarify certain aspects of the trace-element problem, but more detailed explanation must await further study with other techniques.

As already mentioned, the bulk of the content of most trace elements occurs within the unweathered crystal lattices of the rock-forming minerals, where it is fixed and unavailable. In studying distribution in soil profiles, it is necessary to consider the effects of pedological processes in modifying the course or rate of weathering, in effecting subsequent translocation, in bringing about size-sorting of the mineral constituents within the profile and in modifying the processes of formation of clay minerals. In assessing such effects by extraction methods, it must be remembered that increased amounts extracted from any horizon can be evidence either of weathering *in situ* and possible incipient translocation from that horizon or of accumulation of material in an extractable form in an horizon of deposition. Material which has been translocated and fixed in a new horizon is, however, not necessarily readily extractable. Changes in the clay minerals with which the trace elements become associated may either increase or decrease the ease of extraction.

(a) Extractable trace elements in freely drained arable soils

The soils of Scotland are typically podzolic in nature, with brown forest soils of low base status occurring on the more basic parent materials. The characteristic cultivated soil is slightly podzolized, and consideration will be given first to the extractable trace elements in such soils; in Table 2 will be found results for acetic acid and in some instances ammonium acetate extraction of typical cultivated soils, all reasonably freely drained. Two further examples are included in Table 4, in which they are compared with neighbouring soils in which the drainage is less free.

These profiles illustrate the normal rather than the extreme ranges of contents of extractable trace elements found in freely drained Scottish arable soils, the figures calling for little comment except to remark that, for instance, in cobalt-deficient soils, the Co content of the surface horizon may be considerably lower than any reported here. Contents lower than 0·1 p.p.m. acetic acid extractable Co have been observed in soils of granitic or arenaceous Old Red Sandstone origin in areas where cobalt deficiency in sheep occurs. If any tendency is obvious in the profiles it is generally, as might have been anticipated, for a gradual fall in trace-element extraction with depth. This occurs irrespective of clay content, which falls from 25 to 5 per cent. in profile 2A and rises from 13 to 21 per cent. in profile 2B, the other profiles being intermediate in behaviour. The acidity of the soils in question always lies within the pH-range 5·5–6·5, with exchangeable Ca falling from 14·1 to 5·5 m.e. per 100 g. in profile 2D and from 2·4 to 0·5 in profile 2C, these again being the extreme instances.

TABLE 2

Extractable Trace-elements in Typical Scottish Freely-drained Arable Soils
(expressed as parts per million removed from air-dry soil)

2A. *Cultivated podzol, freely drained, on light textured Old Red Sandstone till, Kincardineshire.*
Strathfinella association, Strathfinella Series.

Horizon	Depth (in.)	Soluble in 2·5 % acetic acid												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	0–8	1,070	0·40	0·25	0·24	< 5	114	< 0·02	0·26	0·69	< 0·2	< 0·13	0·16	5·4
B_1	13–19	2,520	0·20	0·41	0·07	30	19	< 0·05	0·16	< 1·0	< 0·5	< 0·30	0·21	7·4
B_2	22–26	2,230	0·12	0·62	0·23	80	5·9	< 0·04	0·19	< 0·9	< 0·5	0·98	0·38	6·7
C	38–44	1,590	0·07	0·19	0·11	15	8·5	< 0·03	0·08	< 0·6	< 0·3	0·35	0·14	4·7

2B. *Cultivated podzol, freely drained, on granitic till, Aberdeenshire.*
Countesswells association, Countesswells Series.

Horizon	Depth (in.)	Soluble in 2·5 % acetic acid												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	0–10	1,000	0·34	0·15	0·31	15	73	< 0·02	0·62	0·29	< 0·1	0·39	0·41	6
B_1	12–14	930	0·14	0·08	0·26	55	51	< 0·02	0·10	0·43	< 0·1	0·65	0·68	6
B_1	18–20	700	0·05	0·11	0·53	45	7·4	< 0·02	0·13	0·26	< 0·1	0·40	0·06	< 5
B_2	24–30	320	0·09	0·08	0·75	80	6·3	< 0·02	0·06	0·20	< 0·1	0·07	0·05	< 5
Cg	37–41	400	0·17	0·11	0·48	25	6·8	< 0·02	0·10	0·35	< 0·1	0·49	0·08	< 5

Horizon	Depth (in.)	Soluble in neutral normal ammonium acetate												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	0–10	< 50	0·02	0·01	..	< 5	..	0·03	0·03	0·54	< 0·04	0·03	0·03	< 2
B_1	12–14	< 50	0·01	0·01	..	5	..	< 0·01	0·01	0·16	< 0·04	0·06	0·02	< 2
B_1	18–20	< 50	0·01	< 0·01	..	10	..	< 0·01	0·01	0·12	< 0·04	< 0·02	0·01	< 2
B_2	24–30	< 50	0·03	< 0·01	..	< 5	..	0·01	0·02	0·11	< 0·04	0·01	0·02	< 2
Cg	37–41	< 50	0·02	< 0·01	..	< 5	..	< 0·01	0·01	0·11	< 0·04	< 0·02	0·01	< 2

2C. *Cultivated brown forest soil (low base status), freely drained, on mixed acidic and basic igneous till, Banffshire.*
Tarves association, Tarves Series.

Horizon	Depth (in.)	Soluble in 2·5 % acetic acid												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	0–6	1,360	0·96	0·55	1·2	25	130	< 0·03	1·3	0·65	< 0·1	0·15	0·12	5
B_1	17–21	3,810	0·42	1·30	0·71	80	24	< 0·07	0·58	< 0·22	< 0·4	1·9	0·48	< 15
B_1	25–29	2,960	0·23	0·90	0·50	50	14	< 0·06	0·29	< 0·17	< 0·3	1·3	0·33	< 12
B_2	36–40	2,430	0·21	0·55	0·22	15	8·2	< 0·05	0·22	< 0·14	< 0·2	0·45	0·15	< 10
C	50–56	1,090	0·36	0·30	0·34	10	16	< 0·02	0·13	0·15	< 0·1	< 0·04	0·17	< 4

2D. *Cultivated brown forest soil (low base status), freely drained, on till derived from mixed (andesitic?) lavas, Ayrshire.*
Darleith association, Darleith Series.

Horizon	Depth (in.)	Soluble in 2·5 % acetic acid												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	2–8	1,850	0·84	0·40	0·38	10	87	< 0·01	0·40	< 0·7	< 0·4	< 0·2	0·05	< 6
B_2	13–19	4,950	0·17	0·71	0·13	< 5	15	< 0·10	< 0·10	< 1·9	< 1·0	< 0·6	< 0·10	< 14
B_2–C	24–30	3,730	0·10	0·24	0·11	< 5	6·9	< 0·07	< 0·07	< 1·3	< 0·7	< 0·4	< 0·07	< 11
C	36–42	2,450	0·36	0·24	0·24	< 5	13	< 0·05	0·21	< 1·0	< 0·5	< 0·3	0·10	< 7

TABLE 2 (*cont.*)

2E. *Cultivated brown podzolic soil, freely drained, on serpentine till, Aberdeenshire. Leslie association, Leslie Series.*

Horizon	Depth (in.)	*Soluble in 2·5 % acetic acid*												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	2–7	1,110	4·2	0·31	0·06	125	6·5	<0·02	104	0·24	<0·1	0·70	0·21	18
B_1	8–12	660	11·0	1·10	0·19	80	85	<0·03	100	<0·6	<0·1	0·22	0·02	11
B_2	18–22	350	8·2	0·39	0·30	40	116	<0·02	74	<0·5	<0·1	0·11	<0·02	<5
B–C	26–30	250	6·6	0·60	0·26	25	115	<0·02	60	<0·4	<0·1	0·15	<0·02	<5
C	38–43	240	6·5	0·63	0·25	20	126	<0·02	61	<0·4	<0·1	0·10	<0·02	<5

Horizon	Depth (in.)	*Soluble in neutral normal ammonium acetate*												
		Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
S	2–7	<50	0·43	0·10	..	20	..	0·01	7	<0·15	<0·04	0·23	0·03	<2
B_1	8–12	<50	0·52	0·04	..	5	..	<0·01	32	<0·15	<0·04	0·01	<0·01	<2
B_2	18–22	<50	0·19	0·01	..	5	..	<0·01	21	<0·15	<0·04	0·10	<0·01	<2
B–C	26–30	<50	0·18	0·01	..	<5	..	<0·01	18	<0·15	<0·04	<0·01	<0·01	<2
C	38–43	<50	0·13	0·01	..	<5	..	<0·01	14	<0·15	<0·04	<0·01	0·01	<2

A value of 10 m.e. Ca per 100 g. soil is equivalent to 2,000 p.p.m., and it is interesting to note that in these freely drained soils, apart from that of granitic origin, the acetic acid extractable Al is of a similar order, and much higher than any of the other elements reported. The Ca is all truly exchangeable, while less than 50 p.p.m. Al is removed by ammonium acetate at pH 7. Whether or not the remainder is exchanged and subsequently precipitated at pH 7 cannot be established from the results available.

The amounts of the other trace elements extracted by acetic acid are much smaller. The levels of Fe, Mn, and Zn are generally between 1 and 100 p.p.m., a value approached also by Co and Ni in some soils of ultrabasic origin. Contents below 1 p.p.m. are normal for most other elements, and may be less than one-hundredth of this even for biologically important Mo. The amounts extracted by ammonium acetate are generally much smaller than those with acetic acid, exceptions being Mo and Pb in certain surface horizons.

Soil 2E, of ultrabasic origin, is that for which total contents are presented in Table 1A, and it is interesting to compare the relative values, particularly in the surface horizon. The marked reductions in total contents of Co and Ni are less obvious in the extracts; for Mn on the other hand with acetic acid extraction the effect is much more apparent. This low surface content of extractable Mn, compared also with the other soils in Table 2, is possibly related not to surface leaching but to the high organic matter content of the surface soil—almost 40 per cent. loss on ignition compared with around 10 per cent. in the other profiles.

In general, the amounts of extractable trace elements are as anticipated, Co and Ni being lower in the soils derived from granite and sandstone than in those of basic or ultrabasic origin. The higher content of Pb in the granitic soil is also in accordance with expectation.

(*b*) *Extractable trace elements in podzolized soils*

The greatest pedological effects on trace-element distribution might be anticipated in podzols with iron pan. Results for the acetic acid extraction of four profiles of varying parent material are quoted in Table 3. In two of the samples reported, the pan was discontinuous and could not be sampled by the surveyors to whom we are indebted for the soil samples.

The typical diagnostic characteristic of podzolization, the accumulation of iron in the upper illuvial horizon, the B_1 pan, is well shown in profile 3A on a granitic parent material. This is the profile for which total analyses are quoted in Table 1D. A well-developed pan is also present in profile 3B, developed on felsitic lavas in the Southern Uplands. In this profile the increased content of acetic acid extractable iron in the pan is even more marked, being thirty times as great as in the A_2 horizon. The difference in acetic acid extractable aluminium, on the other hand, is barely significant, while there is no evidence of accumulation of extractable Co or Ni in the iron pan, although there may be some removal from the A horizons and perhaps a slight increase in extractable amount in the lower B layers. A marked increase in acetic acid extractable Cu occurs in this iron pan. In both profiles the highest content of extractable V and Ti is observed in the A_2 horizon—possibly evidence of mobilization and impending translocation.

Profile 3C has been developed on arenaceous Old Red Sandstone parent material, relatively low in all trace elements. This podzol had only a thin discontinuous pan, and here the accumulation of extractable Fe in the B_2 horizon is more obvious than in soils with a well-developed pan. There may be a suggestion of accumulation of extractable Co, Cr, V, and Ti in this instance, but only for Cr is the effect as marked as that observed for Fe. Some results are also available for ammonium acetate extraction of this profile. With this reagent there is less evidence of increase in extractable trace elements in the eluvial horizons. It is interesting to note the high level of ammonium acetate extractable Pb in the FH-horizon, which has a loss on ignition of 78 per cent. This suggests the possibility that organically-bound Pb is involved. In this soil a total content of 4 p.p.m. Ge was observed in the surface horizon.

In profile 3D, of andesitic origin, it is interesting to note the accumulation of Ni relative to Co in the surface horizon, probably through plant accumulation. This profile displays an abnormal amount of extractable Fe in the surface horizons and little evidence of accumulation in the B horizon. The mobilization of V in the A horizons is very marked.

All but one of the podzols have low contents of acetic acid extractable Mn in the surface horizons and very low contents in the A_2 and B_1 horizons.

(*c*) *Effect of drainage status on trace-element mobilization*

Under conditions of impeded drainage the factors responsible for the weathering of rock-forming minerals and the formation of clay minerals differ markedly from those operating in freely drained soils. W. A. Mitchell (1955) has pointed out that in Scottish soils derived from rocks

TABLE 3

Extractable Trace-elements in Scottish Podzols
(expressed as parts per million removed from air-dry soil)

3A. *Peaty gleyed podzol with iron pan, poorly drained above, freely drained below pan, on granitic till, Kincardineshire. Countesswells association, Charr Series.*

Horizon	*Depth (in.)*	*% Loss on ignition*	*% clay*	pH	*Soluble in 2·5 % acetic acid*												
					Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
H	7–9	65·7	..	4·2	875	0·14	0·06	<0·10	25	1·4	<0·03	0·33	<0·7	<0·2	0·31	0·06	26
A_2 g	10–14	5·8	6·3	4·4	695	<0·03	<0·03	0·11	30	<0·8	<0·03	0·21	<0·6	<0·2	0·27	<0·03	<5
A_2 g	17–21	9·5	11·2	4·6	4060	<0·08	0·21	0·13	40	<0·8	<0·08	0·13	<1·6	<0·4	3·5	0·49	<10
B_1	21	..	..	..	5850	<0·12	0·17	0·27	595	0·84	<0·12	<0·12	<2·4	<0·6	0·79	<0·12	<10
B_2	21–25	6·2	12·3	4·9	5550	<0·11	<0·11	0·22	100	3·5	<0·11	<0·11	<2·2	<0·6	1·2	<0·11	<10
B_2–C	31–36	3·4	6·3	4·8	3130	0·12	0·15	0·13	10	4·2	0·14	0·14	0·9	0·3	0·44	0·08	<10
C	40–46	3·1	7·6	4·9	2920	0·09	<0·06	0·24	<5	<0·8	0·09	0·29	1·8	<0·3	0·12	0·06	<10

3B. *Peaty podzol with thin iron pan freely drained, on till derived from felsitic lavas, Roxburghshire. Sourhope association, Coxcie Series.*

Horizon	*Depth (in.)*	*% Loss on ignition*	*% clay*	pH	*Soluble in 2·5 % acetic acid*												
					Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
F	1–1·5	..	..	..	285	0·16	0·04	0·0	15	45	<0·02	0·43	1·3	<0·1	<0·04	0·04	23
H	4–8	89·6	..	3·9	390	0·30	0·06	0·0	20	47	<0·03	0·86	1·2	<0·1	<0·06	0·05	28
A_1–A_2	10–12	15·5	6·8	4·5	1785	0·07	0·53	0·0	30	2·2	<0·05	0·30	<0·5	<0·3	3·5	0·72	<10
B_1	12·5	..	..	..	2250	<0·09	0·83	0·47	940	3·8	<0·09	0·14	<0·9	<0·4	0·51	0·05	<10
B_2	13–17	4·9	11·6	5·0	3060	0·31	0·68	0·04	60	54	<0·06	0·09	<0·6	<0·3	0·22	0·07	<10
B_2–C	24–28	4·1	10·5	4·9	4120	0·28	0·34	0·05	55	28	<0·08	0·29	<0·8	<0·4	1·3	0·18	<10

TABLE 3 (*cont.*)

3C. *Podzol with discontinuous thin iron pan, freely drained, on till derived from arenaceous and conglomerate beds of Old Red Sandstone age, Angus*
Strathfinella association, Strathfinella Series.

Horizon	Depth (in.)	% Loss on ignition	% clay	pH	Soluble in 2·5 % acetic acid												
					Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
FH	1–3	77·7	..	3·9	370	0·25	0·15	0·71	20	15	<0·02	0·52	1·9	<0·2	0·33	0·23	46
A_2	3–6	8·7	12·6	4·1	735	0·06	0·12	0·03	55	<0·8	<0·02	0·23	1·4	<0·2	1·5	0·25	7
B_1	6–9	9·3	17·9	4·6	2820	0·09	0·52	0·04	175	<0·8	<0·06	0·21	1·9	<0·6	2·1	0·55	<10
B_2	9–12	5·8	16·9	4·6	3310	0·08	0·39	0·05	115	0·84	<0·07	<0·07	<1·3	<0·7	0·52	0·28	<10
B_3–C	20–24	2·6	14·0	4·8	3280	0·13	0·18	0·04	15	9·2	<0·06	<0·06	<1·3	<0·6	<0·4	<0·06	<10

Horizon	Depth (in.)	% Loss on ignition	% clay	pH	Soluble in neutral normal ammonium acetate												
					Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
FH	1–3	77·7	..	3·9	..	0·05	0·01	..	<2	..	<0·01	0·07	6·3	<0·1	0·25	0·06	6
A_2	3–6	8·7	12·6	4·1	..	0·01	0·02	..	6	..	0·03	0·04	<0·2	<0·1	0·59	0·06	<1
B_1	6–9	9·3	17·9	4·6	..	0·02	0·04	..	16	..	0·01	0·04	<0·2	<0·1	0·82	0·05	<1
B_2	9–12	5·8	16·9	4·6	..	<0·01	0·05	..	7	..	<0·01	0·03	<0·2	<0·1	0·50	0·01	<1
B_3–C	20–24	2·6	14·0	4·8	..	<0·01	0·04	..	<2	..	<0·01	0·03	<0·2	<0·1	<0·04	0·01	<1

3D. *Peaty podzol with iron pan, freely drained below pan, on till derived from andesitic lava, Ayrshire.*
Darleith association, Baidland Series.

Horizon	Depth (in.)	% Loss on ignition	% clay	pH	Soluble in 2·5 % acetic acid												
					Al	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sn	T	V	Zn
A_1	2–5	40·5	..	4·8	2550	0·20	0·26	0·24	275	7·8	<0·05	1·3	0·6	<0·2	0·84	0·95	18
A_2 (g)	6–8	23·5	17·8	4·8	4490	0·26	2·5	0·10	140	8·0	<0·09	0·24	<0·9	<0·3	0·47	1·5	<10
B_1	9–12	11·0	19·5	4·9	6900	0·54	1·5	0·24	40	14	<0·14	0·17	<1·4	<0·4	<0·8	0·24	<15
B_2	14–18	6·2	19·1	4·8	6500	0·40	0·88	0·32	<5	11	<0·13	0·07	<1·3	<0·4	<0·8	<0·13	<15
C	22–28	5·4	17·0	4·9	5450	0·28	0·52	0·46	<5	23	<0·11	0·11	<1·1	<0·3	<0·7	0·16	<10
C	33–38	4·7	25·0	5·5	1970	0·18	0·07	0·42	<5	22	<0·04	0·31	<0·4	<0·1	<0·2	0·07	<5

rich in ferromagnesian minerals the clay fraction is dominated by vermiculite or montmorillonite, the former being more prevalent in freely drained and the latter in poorly drained profiles, particularly in the gleyed layers. In soils of acid igneous or sedimentary origin the mineralogical effect of gleying is less obvious. Illite and kaolin are the predominant clay minerals, with an increase in kaolin in the upper layers which is more obvious in the freely drained soils. There are thus adequate mineralogical grounds for anticipating differences in trace-element behaviour in wet soils.

A brief description of the effect of gleying on the content of extractable trace elements in a basic igneous soil (Mitchell, 1955*a*) has provided an explanation of the suggestion by Hill, Toth, and Bear (1953) that cobalt uptake by plants is greater on poorly drained soils. In Table 4A will be found results for acetic acid and ammonium acetate extractions of closely adjacent profiles developed on basic igneous parent material at three drainage levels, while in Table 4B corresponding results for soils developed on a Silurian shale are presented.

On the soils of the Insch association (Glentworth, 1954) on olivine gabbro the increased ease of extraction, in the gleyed soils, of Co, Ni, Fe, Cu, Mn, and V in one or both of the extractants can be observed (Table 4A), the soil with imperfect drainage generally giving an intermediate value. It is particularly interesting to note that up to 70 per cent. of the Co and Ni extractable by acetic acid from the gleyed layers of the very poorly drained soil is taken out by neutral ammonium acetate, although generally in freely drained soils there is a tenfold ratio, as is in fact found in the surface layers of these profiles (cf. Mitchell, 1945). With V, on the other hand, the increased solubility shown with acetic acid is not found with ammonium acetate at pH 7. The amount of Co extracted by acetic acid approaches 50 per cent. of the total content (the values in Table 1B relate to a comparable profile intermediate between the freely and poorly drained soils discussed here). In the bottom layer of the very poorly drained soil, one-half of the Co and Ni and one-tenth of the Fe extracted by acetic acid is soluble in water: in the layer immediately above, the ratio for Co is one-thirty-fifth. The actual Co, Ni, and Fe values in p.p.m. are:

	Co		Ni		Fe	
Depth in inches	25	38	25	38	25	38
Acetic acid soluble	2·1	18	3·9	22	75	2,500
Ammonium acetate soluble . .	0·76	13	1·1	15	<5	<5
Water soluble	0·06	9·5	0·16	10·4	50	265

As the total Co and Ni contents show little or no increase in the lowest horizon, despite the marked increase in the extractable amounts, it seems reasonable to postulate that the Co and Ni are being released *in situ* by breakdown of the ferromagnesian minerals in which they are initially bound. In the horizons with high extractable contents they are then held in a readily extractable form partly by adsorption, perhaps on montmorillonite, and partly in soluble form, possibly as sulphate.

TABLE 4

Effect of Drainage Conditions on Trace-element Mobilization in Two Scottish Soil Associations

4A. ***Profiles developed on Olivine Gabbro Till, Aberdeenshire***

Insch association, Insch Series, freely drained FD
" " Myreton Series, poorly drained PD
" " Mosstown Series, very poorly drained VPD

Extractant: 2·5 % acetic acid HAc
neutral normal ammonium acetate NH_4Ac

Amounts removed from air-dry soil expressed in parts per million

Approx. depth in in.		6		12		17		25		38	
Extractant		HAc	NH_4Ac	HAc	NH_4Ac	HAc	NH_4Ac	HAc	NH_4Ac	HAc	NH_4Ac
Element	*Series*										
Al	FD	2,500	..	4,600	..	3,600	..	3,300	..	1,500	..
	PD	880	..	795	..	845	..	655	..	365	..
	VPD	550	..	840	..	475	..	410	..	765	..
Ca	FD	..	2,880	..	195	..	230	..	1,290	..	1,665
	PD	..	1,090	..	730	..	1,200	..	1,145	..	665
	VPD	..	956	..	1,265	..	435	..	1,430	..	1,150
Co	FD	1·3	0·04	0·52	0·02	0·17	0·01	0·14	0·01	0·15	0·02
	PD	1·9	0·10	0·77	0·07	1·2	0·13	2·7	0·20	3·6	0·63
	VPD	1·5	0·08	2·5	0·37	2·2	0·37	2·1	0·76	18	13
Cr	FD	0·24	0·03	0·43	<0·01	0·25	<0·01	0·23	<0·01	0·05	<0·01
	PD	0·17	<0·01	0·22	0·01	0·17	<0·01	0·18	0·01	0·13	0·02
	VPD	0·18	<0·01	0·14	<0·01	0·25	<0·01	0·14	<0·01	0·32	<0·01
Cu	FD	0·13	..	0·21	..	0·28	..	0·17	..	0·16	..
	PD	0·15	..	0·10	..	0·70	..	0·96	..	1·82	..
	VPD	0·63	..	1·4	..	0·33	..	2·7	..	6·2	..
Fe	FD	20	<5	20	<5	15	<5	15	<5	15	5
	PD	15	<5	20	<5	25	<5	15	<5	450	<5
	VPD	25	5	500	5	20	<5	75	<5	2500	<5
Mg	FD	..	153	..	32	..	35	..	124	..	316
	PD	..	119	..	178	..	276	..	405	..	539
	VPD	..	132	..	240	..	128	..	425	..	444
Mn	FD	..	8·5	..	1·0	..	1·0	..	2·1	..	1·6
	PD	72	11	22	2·4	19	3·1	32	6·0	74	54
	VPD	..	70	..	33	..	16	..	>100	..	>100
Ni	FD	1·3	0·11	0·36	0·02	0·31	0·01	0·15	<0·01	0·12	<0·01
	PD	2·2	0·17	1·4	0·10	2·4	0·46	3·3	0·96	5·0	1·2
	VPD	4·1	0·22	4·2	0·44	6·7	0·59	3·9	1·1	22	15
V	FD	0·15	0·01	<0·09	<0·01	<0·07	<0·01	0·06	<0·01	<0·03	<0·01
	PD	0·46	0·01	0·92	<0·01	0·34	<0·01	0·13	<0·01	0·44	<0·01
	VPD	1·2	0·02	3·8	0·03	1·1	0·04	1·7	0·04	1·7	0·02
pH	FD	6·2		5·4		5·3		5·3		5·5	
	PD	5·8		5·7		5·9		6·0		5·7	
	VPD	6·4		5·4		6·4		5·8		4·5	
		Base exchange capacity in m.e. per 100 g.									
	FD	28		11		7		18		18	
	PD	8		8		12		13		14	
	VPD	12		19		7		15		21	

TABLE 4 (*cont.*)

4B. *Profiles developed on Silurian Slate, Roxburghshire.*

Ettrick association, Linhope Series, freely drained FD
" " Ettrick Series, poorly drained PD
" " Hardlee Series, very poorly drained VPD
Extractant: 2·5 % acetic acid HAc
neutral normal ammonium acetate NH_4Ac

Amounts removed from air-dry soil expressed in parts per million

Approx. depth in in.			5	8	14	18	25	36
Element	*Extractant*	*Series*						
Al	HAc	FD	2,000		2,280	2,100	1,660	1,210
		PD	1,990	1,140	960	550	400	300
		VPD	2,410		1,070	720	500	425
Ca	NH_4Ac	FD	676		152	30	30	152
		PD	218	60	334	1,410	3,480	11,880
		VPD	2,174		360	364	1,130	1,490
Co	HAc	FD	1·5		1·3	0·36	0·25	0·27
		PD	0·43	0·20	0·62	0·73	0·11	0·97
		VPD	1·9		0·27	0·41	0·12	0·87
Cr	HAc	FD	0·53		0·99	0·73	0·34	0·24
		PD	0·09	0·60	0·42	0·18	0·13	0·14
		VPD	0·26		0·96	0·75	0·50	0·43
Cu	HAc	FD	0·19		0·20	0·32	0·29	0·34
		PD	0·54	0·43	0·91	0·70	0·32	0·32
		VPD			1·36	3·89	11·8	12·9
Fe	HAc	FD	20		40	25	20	20
		PD	75	40	30	15	<5	35
		VPD	80		95	70	75	210
Mg	NH_4Ac	FD	64		27	20	15	29
		PD	41	24	46	73	146	171
		VPD	352		73	66	102	78
Mn	HAc	FD	144		9·7	22	34	16
		PD	3·1	5·6	34	67	104	168
		VPD			1·3	7·7	8·7	153
Ni	HAc	FD	0·38		1·1	0·50	0·19	0·15
		PD	1·1	0·27	0·34	0·80	2·1	1·4
		VPD	4·3		0·98	0·97	0·54	1·4
Pb	HAc	FD	<0·12		<0·14	<0·12	<0·10	0·19
		PD	0·78	0·18	0·23	0·06	0·13	0·55
		VPD	7·6		1·0	1·9	1·9	0·60
Sn	HAc	FD	0·13		0·50	0·25	0·07	0·40
		PD	<0·20	<0·12	<0·10	<0·10	< 0·10	< 0·10
		VPD	<0·24		<0·11	<0·08	< 0·10	< 0·10
V	HAc	FD	0·05		0·06	0·06	0·09	0·08
		PD	0·18	0·06	0·05	0·05	0·08	0·04
		VPD	1·2		2·0	1·6	1·9	4·3
pH		FD	5·0		5·2	5·2	5·3	5·3
		PD	4·8	5·3	5·2	5·6	7·3	8·3
		VPD	4·6		5·5	5·6	5·6	6·0
Base exchange capacity in m.e. per 100 g.								
		FD	22		12	7	5	6
		PD	23	8	9	12	19*	61*
		VPD	67		10	4	7	8

* free lime

The two lowest horizons contain respectively 125 and 3,660 p.p.m. SO_4 soluble in water. The relative amounts of Fe and SO_4 indicate that in both horizons much of the acetic acid extractable Fe could be present as $FeSO_4$, although it must be remembered that there is over 400 p.p.m. ammonium acetate extractable Mg in both horizons and 400–800 p.p.m. extractable Al. The lower apparent extraction of Fe compared with Co and Ni in ammonium acetate and water from the lowest layer is probably due to subsequent precipitation of hydroxide at nearly neutral pH.

There is evidence of the presence of only a small amount of sulphide in the gleyed horizons after air-drying, while the water extract of the air-dried sample from the lowest horizon showed the presence of ferrous iron with only a trace of ferric iron. It seems improbable that the simple process of air-drying would convert large amounts of $S^{=}$ to SO_4 with little or no conversion of Fe^{++} to Fe^{+++}, hence the conclusion that soluble sulphates are present in the gleyed horizon of this soil.

The amount of aluminium extracted by acetic acid is much smaller in the poorly drained soils. This effect differs from that for most other elements in that it is apparent in all horizons of the basic igneous profile, but in this respect the behaviour of V, Cu, and Mn may be noted. The high content of acetic acid soluble Al in well-drained soils derived from basic igneous rocks has been found to be particularly marked in those of basaltic origin, and difficulties may arise in carrying out trace-element concentration prior to spectrochemical analysis (Mitchell, 1948) because of this. The amount of extractable Al is probably related to the manner and rate of formation of secondary clay minerals. A similar effect has been reported by Williams and Saunders (1956) for NH_4F-extractable Al. The high contents of extractable Cu and Mn in the poorly drained soil may well be of practical importance.

It is interesting to note that in these soils only slight effects are noted for Ca and, in particular, for Mg which must be derived from the same primary minerals as Fe, Co, and Ni. The constancy of the base exchange capacity in the lower horizons, irrespective of drainage status, is also worthy of notice.

In the soils derived from the Silurian slate (Table 4B), pedological descriptions and analyses of which have been reported by Muir (1956, profiles 4, 40, 60), the qualitative changes are similar in nature to those just considered, but their relative magnitudes are somewhat different, presumably because of the different mineral species which are undergoing weathering. Once again the lower extraction of aluminium from the poorly drained profiles is obvious, but is not apparent in the surface horizon. In this sequence of soils the poorly drained member is classified as a non-calcareous gley, but the extractable calcium and pH value in the lowest layers are both exceedingly high. Low extraction of certain trace elements, notably Cu, Cr, and V, from this soil may be related to high calcium content counteracting the effect of gleying, or affecting the extraction. In general, increased mobilization of Co, Ni, V, Pb, Fe, and Cu occurs in the poorly drained soils.

The magnitude of the effect of impeded drainage is such that minor

variations observed in extractable trace-element contents in what would normally be regarded as freely drained soils may be attributable to this effect. Thus in Table 2 the relatively very slight increases in certain elements in the bottom layers in profiles 2B, 2C, and 2D may well be due to slight changes in drainage status. This effect would appear to make the detailed study of other factors affecting extractable trace elements exceedingly difficult under conditions of marked local variations in drainage such as are common in Scotland. The widespread occurrence of indurated horizons in many soils may be a factor of importance in view of their effect on drainage.

Certain practical consequences of variation in drainage have been demonstrated by Mitchell, Reith, and Johnston (1957) who have shown obvious increases in plant uptake on poorly drained areas, particularly with Co and Ni, but also to some extent with Mo, Cu, and Mn. Areas of Ni toxicity in plants and of Mo toxicity in animals in north-east Scotland have also been found to be associated with conditions of restricted drainage at some stage of the soil development.

Discussion and Conclusions

The findings indicate the major importance of geological parent material in determining soil trace-element status. Thus the soil association rather than the soil series defines the potential trace-element behaviour of any soil, confirming the validity of the units which are being mapped. Generally, pedological factors have little or no effect on the total trace-element content of individual horizons, although for certain elements, such as Pb and Ge, pronounced concentration in organic matter rich surface horizons may occur.

The effective trace-element status, in so far as it relates to practical considerations of plant uptake and animal health, is more directly related to the amounts which can readily be removed by one or other of the extractants devised for specific purposes. Certain pedological factors have quite marked influence on the results obtained by these methods. Under Scottish conditions by far the most important is the effect of impeded drainage in gleyed soils. The increased ease of extraction of such biologically important elements as Co, Cu, Mn, Mo, and Zn, as well as potentially toxic elements such as Ni, is very marked in poorly drained horizons, particularly in soils derived from rocks with high contents of ferromagnesian minerals.

Impeded drainage may in extreme instances mobilize up to 50 per cent. of the total content of the element in question, while the effects of other pedological processes such as podzolization are, if obvious at all by the methods employed, of a much smaller order. Hence, minor local changes in drainage conditions are quite liable to obscure effects of other factors. It is possibly pertinent to note that in zones of trace-element accumulation in Scottish peats (Mitchell, 1954) the elements which are most affected are those which display increased mobilization in mineral soils in conditions of poor drainage, and it seems reasonable to suggest that such accumulation may have occurred as a result of movement from such poorly drained mineral soils adjoining or underlying the peat

deposits. The magnitude of the effect is difficult to explain in any other way.

In well-drained agricultural soils, and in typical podzols, there is normally a decrease in extractable trace elements from the surface horizon downwards, although in podzols a slight, although unexpectedly small, increase in the B horizon may be apparent with certain elements. In poorly drained soils the maximum extraction generally occurs in the gleyed layers at considerable depth.

The findings indicate an increased availability of many trace elements in poorly drained soils, but do not necessarily mean that artificial drainage of such soils will reduce this availability. The long-term effect of such improvement can only be established by experimental investigation.

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REFERENCES

Butler, J. R. 1954. Trace-element distribution in some Lancashire soils. J. Soil Sci. **5**, 156.

Connor, J., Shimp, N. F., and Tedrow, J. C. F. 1957. A spectrographic study of the distribution of trace elements in some podzolic soils. Soil Sci. **83**, 65.

Gammon, N., Henderson, J. R., Carrigan, R. A., Caldwell, R. E., Leighty, R. G., and Smith, F. B. 1953. Physical, spectrographic and chemical analyses of some virgin Florida soils. Bull. Fla. Agric. Exp. Sta. 524.

Glentworth, R. 1954. The soils of the country round Banff, Huntly and Turriff. Mem. Soil Surv. Gt. Brit. (Scotland). Edinburgh, H.M.S.O.

Goldschmidt, V. M. 1937. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. 655.

—— 1954. Geochemistry. Oxford, Clarendon Press.

Hill, A. C., Toth, S. J., and Bear, F. E. 1953. Cobalt status of New Jersey soils and forage plants, and factors affecting the cobalt content of plants. Soil Sci. **76**, 273.

Kovda, V. A., and Vasilyevskaya, V. D. 1958. A study of the minor element content in soils of the Amur river region. Pedology, No. 12, 68.

Lounamaa, J. 1956. Trace elements in plants growing wild on different rocks in Finland. A semi-quantitative spectrographic survey. Ann. (bot.) Soc. Zool.-Bot. Fenn. Vanamo, **29**, No. 4.

Mason, B. 1952. Principles of Geochemistry. New York, Wiley.

McKenzie, R. M. 1956. Trace element distribution in some South Australian red-brown earths. C.S.I.R.O. (Aust.), Div. Soils, Div. Rep. 9/56.

—— 1957. The distribution of trace elements in some South Australian red-brown earths. Aust. J. Agric. Res. **8**, 246.

Mitchell, R. L. 1945. Cobalt and nickel in soils and plants. Soil Sci. **60**, 63.

—— 1948. Spectrographic analysis of soils, plants and related materials. Commonw. Bur. Soil Sci., Tech. Commun. 44.

—— 1954. Trace elements in Scottish peats. Proc. Int. Peat Symp. Dublin, Section B3.

MITCHELL, R. L., 1955*a*. Trace elements in Chemistry of the Soil. A.C.S. Monograph No. 126. New York, Reinhold, p. 253.

—— 1955*b*. Spectrochemical analysis of plants and soils. Proc. Soil Sci. Soc. Fla., **15**, 12.

—— 1957. Spectrochemical methods in soil investigations. Soil Sci. **83**, 1.

—— and SCOTT, R. O. 1957. The application of spectrochemical methods to agricultural problems. Appl. Spectroscopy, **11**, 6.

—— REITH, J. W. S., and JOHNSTON, I. M. 1957. Trace-element uptake in relation to soil content. J. Sci. Fd. Agric. **8**, S51.

MITCHELL, W. A. 1955. A review of the mineralogy of Scottish soil clays. J. Soil Sci. **6**, 94.

MUIR, J. W. 1956. The soils of the country round Jedburgh and Morebattle. Mem. Soil Surv. Gt. Brit. (Scotland). Edinburgh, H.M.S.O.

NOCKOLDS, S. R., and MITCHELL, R. L. 1948. The geochemistry of some Caledonian plutonic rocks: a study in the relationship between the major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edinb. **61**, 533.

RANKAMA, K., and SAHAMA, T. G. 1950. Geochemistry. Chicago, University of Chicago Press.

SWAINE, D. J. 1955. The trace-element content of soils. Commonw. Bur. Soil Sci., Tech. Commun. 48.

TILLER, K. G. 1957. The geochemistry of basaltic tuff and basalt and associated soils in the Mt. Burr area of S.E. South Australia. C.S.I.R.O. (Aust.), Div. Soils, Div. Rep. 3/57.

VINOGRADOV, A. P. 1957. Geochemistry of Rare and Dispersed Chemical Elements in Soils. Moscow, Akad. Nauk, S.S.S.R.

WAGER, L. R., and MITCHELL, R. L. 1951. The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland. Geochim. et Cosmoch. Acta, **7**, 129.

WALSH, T., RYAN, P., and FLEMING, G. A. 1956. Cobalt deficiency in relation to weathering processes in soils. Int. Congr. Soil Sci., Rapp. Comm. II, 771.

WEDEPOHL, K. H. 1956. Untersuchungen zur Geochemie des Bleis. Geochim. et Cosmoch. Acta, **10**, 69.

WILLIAMS, E. G., and SAUNDERS, W. M. H. 1956. Significance of particle-size fractions in readily soluble phosphorus extractions by the acetic, Truog, and lactate methods. J. Soil Sci. **7**, 189.

WRIGHT, J. R., LEVICK, R., and ATKINSON, H. J. 1955. Trace element distribution in virgin profiles representing four great soil groups. Proc. Soil Sci. Soc. Amer. **19**, 340.

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CHEMICAL STUDIES OF PODZOLIC ILLUVIAL HORIZONS

IV. THE FLOCCULATION OF HUMUS BY ALUMINIUM

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Summary

A study of the effects of pH and of carbon/aluminium ratio on the flocculation of podzol humus by aluminium is reported. Portions of resin-treated humus extracts were adjusted to selected pH values (which varied from 1·8 to 7·0) and mixed with equal volumes of $AlCl_3$ solutions at the same initial pH. The C/Al ratios employed were varied from 1·5 to over 20.

At C/Al ratios of 16, using B-horizon humus from an Australian podzol, complete precipitation of C and Al occurred only at pH 4–4·5, i.e. at about the precipitation pH of hydrous aluminium oxide. As the pH was decreased below 4, increasing amounts of C (up to 25 per cent. of that added) and Al (up to 95 per cent.) remained in the supernatant liquid. As the pH was increased above 4·5, all, or nearly all, the added C and Al remained unflocculated. At C/Al ratios of 20 or more, no precipitation of either constituent was found at any pH employed. At a C/Al ratio of 16, only partial precipitation of humus and Al occurred which was maximal at pH 2·5. Similar results were obtained for humus from a New Zealand podzol although it was less sensitive to flocculation.

After mixing the two phases, changes in pH occurred which were independent of C/Al ratio, degree of flocculation, or humus type, but which depended on the mean pH of the C and Al systems before mixing. Negative pH changes were recorded below pH 4·5 while above this value positive differences were found. A detailed analysis of these changes suggested the participation of polymeric hydroxy-aluminium complexes in humus flocculation at pH 3·5–4·5, whereas below pH 3·5 flocculation is probably brought about by free Al ions. Evidence is presented for the exchange of humus 'anions' for hydroxyl on the surface of freshly formed Al hydrous oxide at pH values over 4·5.

A brief study of the sorption of podzol humus by Al-bentonite and by Na-H-bentonite is described. Sorption by Al-clay was maximal and complete from pH 2·0 to pH 3·0, but above this increasing amounts of humus remained unsorbed. Interpretation of the pH changes in these systems was complicated by lack of equilibrium conditions. Pure H-clays (prepared by resin treatment of clay suspensions) showed decreasing sorption from 50 per cent. at pH 2 to practically zero at pH 4·5 or greater. It is suggested that sorption of organic matter by clays in acid soils is facilitated by the presence of exchangeable or surface-sorbed Al.

Humus suspensions showed considerable deflocculating properties towards H- and Al-clays. This factor may be important in clay migration in soils.

Introduction

Evidence presented in the previous paper of this series (Martin and Reeve, 1958) suggested that humus found in the B horizon of a number of podzols was immobilized by the formation of electrostatic bonds with metal ions, rather than by the participation of co-ordinate linkages

between the latter and donor sites on the humus molecule. It was also suggested that, at the pH value normally found in podzol B horizons, aluminium ions were primarily concerned in the precipitation of the organic matter since free ferric ions could not operate above pH 3·0. A detailed investigation of the relative flocculating powers of aluminium and iron (ferrous and ferric) towards humus was therefore undertaken in an attempt to contrast more clearly the flocculating behaviour of the two ionic species. The present paper is confined to a study of the precipitation of humus by aluminium both as free ions and as exchangeable ions on the surface of clay minerals; the effects of ferric and ferrous iron, and of nickel, will be reported in a later communication.

The mutual flocculating action of sesquioxides and humus has been studied in particular by Aarnio (1913), Mattson (e.g. 1931), and Deb (1949). It is important at this stage to consider the practical details of the experimental technique employed by each of these authors, with particular reference to (*a*) type of humus, (*b*) the form in which metal ions or 'hydroxides' were used for flocculation, and (*c*) the degree of pH control achieved in the respective systems.

(*a*) Peat was a favourite source of colloidal humus in many cases. Both Mattson (1931) and Aarnio used it exclusively: Deb also used peat, but extended his observations to other sources including podzol B humus. Peat has obvious advantages with respect to quantity and ease of extraction, but it does not necessarily compare with the humus reputed to be active in podzolization. For obvious reasons, translocated podzol humus is the most appropriate source of organic matter in flocculation studies, and the extraction techniques described previously were used to advantage in the present work.

(*b*) Both Aarnio and Deb used dialysed, colloidal, ferric hydrous oxide sols as metal flocculant, and Aarnio also employed colloidal aluminium hydroxide. The justification for the use of sols is, apparently, that such systems have been identified in drainage water from soils, suggesting that they are the principal reactive forms in which these metals can exist in nature. The use of sesquioxide sols is arbitrary, however, since it is by no means certain that this particular physical manifestation is actually that arising from the decomposition of soil minerals. It is particularly difficult to conceive the means by which colloidal sols of Fe or Al oxides are produced from indurated sesquioxides which are common constituents of the parent material of many podzols.

By contrast, Mattson employed solutions of aluminium and ferric chlorides as metal flocculant. From a consideration of Mattson's general theory of isoelectric precipitates, it is clear that at pH values lower than the isoelectric point of the metal 'hydroxide', the individual micelles tend to acquire a surface positive charge arising from the formation of the free metal ion by protolysis. As these positive centres are presumably the active ones in flocculation of the negatively charged humus particles, there seems little difference in this regard between a sol and a metal salt 'solution' at the same pH. At pH values greater than the I.E.P. it is likely that maximal effects towards humus would be revealed

by a freshly precipitated 'hydroxide' owing to its initially large surface area; this was attained in the present experiments by mixing the freshly adjusted metal salt immediately with the humus phase. The effect of ageing metal 'hydroxides' on their flocculating properties was not investigated here as it was these maximal effects that were of immediate interest; the main interest in the experiments reported below concerned the principles under which humus and the ions of sesquioxide metals interact.

(*c*) Hydrogen-ion concentration has a decided influence on the probable reactive groups of humus and, as suggested above, on Fe and Al solutions or suspensions. The importance of pH control was not apparently recognized by Aarnio. Mattson was particularly concerned with the pH at which his preparations showed zero cataphoretic mobility. Although he adjusted the pH of each mixture by adding NaOH to the humus phase or HCl to the metal chloride solution, his pH measurements were, in fact, made after mixing the two phases, and he does not separately record the pH values of each phase before mixing. Deb endeavoured to control pH by adding HCl to the colloidal ferric iron sol (initial pH = 5·9) only, and assumed that the resulting system had the same pH value as that of the sol. In view of the buffering properties of soil organic matter this seems an unwarrantable assumption. The present authors started from the hypothesis that, just prior to mutual flocculation, the humus and sesquioxide phases would coexist within a comparatively narrow pH range. The most satisfactory pH control would therefore be achieved by separately adjusting each phase to the same apparent pH value before mixing. This is admittedly arbitrary and neglects the influence of the electrical double layer at the humus colloid surface on hydrogen-ion activity, but has the merit of approximating to the situation existing in the soil itself. Another advantage (which was not apparent at first) was that the pH changes on mixing the two isohydric systems revealed to some extent the underlying reactions involved in flocculation and peptization.

The amounts of free aluminium salts found in the soil solution are extremely small. Most of the free aluminium ions, if they occur, are held as exchangeable cations on the surface of clay minerals and probably arise as a consequence of the instability of the hydrogen-saturated materials (Paver and Marshall, 1934; Harward and Coleman, 1954). As a corollary to the use of pure metal solutions for flocculation studies it was necessary to investigate the effect of exchangeable Al on humus precipitation. Since Al-clays form self-flocculating systems it is more precise terminology to refer to the process as sorption of humus rather than mutual flocculation. 'Exchangeable' iron was not studied since it clearly exists at pH values too low to be of practical consequence; hydrous ferric oxide is, however, adsorbed by clay minerals (see Dion, 1944, for a discussion on the forms of iron present in clays) but its sorptive properties were not further considered.

Sorption of humus by pure H-clays (prepared by resin-treatment following the procedure of Harward and Coleman) and of Na-H-clays was also studied for comparative purposes.

Experimental

Technique of flocculation. The technique used throughout was as follows: an aliquot of humus suspension (15–18 ml. containing 10–20 ml. organic carbon as determined by the Walkley and Black method) in a 50-ml. tube was adjusted to within 0·05 unit of the desired pH value by addition of 0·05 N acid or alkali. The total volume of the humus phase was then increased to exactly 20 ml. and the pH value redetermined. In a similar tube, an aqueous solution of aluminium chloride of known concentration was adjusted in a similar manner to the same volume and pH value as that of the humus phase. With experience it was possible to adjust the pH value of one phase to within 0·03 unit of the other although occasionally differences of up to 0·1 unit were recorded, particularly in pH ranges where the metal solution had a low buffering capacity. The choice of C/Al ratio was based on a standard ratio calculated from the weight of organic carbon per unit weight of metal (ether-extractable plus entrained metal) dispersed by acetylacetone (Martin and Reeve, 1957*b*). This was assumed to be the optimum ratio for precipitation in the soil although it clearly varied with soil type. For Beerwah soil, the standard C/Al ratio = 6·0, for Te Kopuru C/Al = 3·0. In calculating the quantity of Al, allowance was always made for the small amounts of this metal entrained in the humus preparation.

The two 20-ml. phases were mixed by repeated transfer from one tube to the other; the pH of the 40-ml. mixture was then determined immediately and after overnight standing. If flocculation occurred overnight, portions of the (uncentrifuged) supernatant solution were carefully withdrawn for the determination of the unflocculated organic carbon and metal present by methods previously described. Where the amounts of organic C were too low for accurate volumetric determination, a colorimetric method was employed for its estimation in which the optical density of suitably diluted aliquots in 0·1 NaOH was compared photoelectrically with standard C preparations obtained from a stock humus suspension from the same source, which had been checked by Walkley and Black titration. Checks were also made on the unflocculated systems in each series; these generally agreed closely in composition with the amounts of metal and organic carbon added.

In a preliminary trial using Beerwah humus and $FeCl_3$ as flocculant, precipitation was strong from pH 1·6 to 3·2 and still considerable at pH 4·7, a surprising result in view of the complete precipitation of ferric ions at about pH 3·0 (Britton, 1956). Further tests showed that this particular organic preparation self-flocculated on addition of dilute HCl below pH 4·0 without any addition of $FeCl_3$. When the original humus suspension was passed through a column of H-'Amberlite', self-flocculation with acid took place only at a lower pH value. Resin treatment increased the C/Al ratio in this case from 7·8 to 50, so it was evident that extraneous Al contained in the Beerwah humus caused self-flocculation at pH 4·0. Clearly, it was essential that humus extracts should be as free as possible from metal ions since the specific flocculating action of each metal species had to be studied without

interference. All the organic matter preparations used subsequently were therefore exhaustively centrifuged and then mechanically shaken overnight with H-'Amberlite' or H-'Dowex', using about 300 ml. wet resin per litre of soil extract. The C/Al ratio was generally increased to 100 or more, indicating the presence of very low amounts of aluminium.

Purified humus extracts from the Beerwah and Te Kopuru soils (Martin and Reeve, 1957 *a*, *b*) were mainly used, but organic matter preparations from other podzols and from a neutral black earth (Waco Clay) from the Darling Downs, Queensland, were also studied in a few cases.

The terms 'pH of precipitation' and 'mean pH value' which are repeatedly used in the text refer to the arithmetic mean of the pH values of the separate phases before mixing, without regard to any subsequent changes in pH that took place after mixing. Strictly the mean hydrogen-ion concentration, subsequently calculated back to the exponential scale, is the more precise, but since the difference in pH between the two phases was small the error involved in calculating the arithmetic mean pH values was negligible.

Sorption of humus by H- and Al-clays. An unpurified sample of Wyoming bentonite, containing about 80 per cent. clay-size material, was employed. A suspension containing 5 g. clay in 250 ml. water was dispersed by shaking with a small amount of NaOH. An excess of dry Zeo-Carb 225 (hydrogen form) was added and the suspension allowed to stand for several days with occasional shaking. It was then poured through glass wool and separate 10 ml. aliquots of the mixed suspension (each containing 200 mg. air-dry clay) were added to each of twelve tubes. To six of these, dilute HCl or NaOH was added to adjust the pH value, giving a range from 2·0 to 5·9. To each of the other tubes, $AlCl_3$ solution was added so that each 200 mg. portion of clay contained 1·19 mg. Al or 66·3 m.e./100 g.; pH values were then adjusted with acid or alkali as before. To each of the 12 tubes, 1 ml. Beerwah humus was added from separate suspensions that had previously been adjusted to the same pH as that of the respective clay suspensions. The C/Al ratio in each tube containing Al was slightly less than 2·0.

Results and Discussion

Flocculation by free aluminium ions

The flocculation of Beerwah humus with Al was studied between C/Al ratios of 1·5 to 24·0; the total amounts of C present in each system (40 ml.) varied from 4 to 16 mg., while Al varied from 1 to 5·5 mg. but was generally 2·7 mg. (i.e. $2{\cdot}5 \times 10^{-3}$ M). Fig. 1 shows the proportion of each constituent remaining in suspension at varying pH values using Beerwah humus at three C/Al ratios.

Precipitation of both metal and organic matter was virtually complete (within a narrow pH range) up to C/Al = 6. At a ratio of 12 (see Fig. 3B of Part V of this series) nearly 40 per cent. of Al was still in suspension at the pH of maximum precipitation, while at C/Al = 16, although some flocculation occurred, it was still incomplete at its maximum value. At

C/Al = 20 or more, no flocculation of either constituent was found over the pH range 1·8–5·0. Maximum precipitation of humus and metal occurred simultaneously at the same pH value at each ratio, and this pH varied inversely with the proportion of C to Al, in agreement with Mattson's theory of isoelectric precipitates (Mattson, 1931) as applied to metal-'humate' preparations.

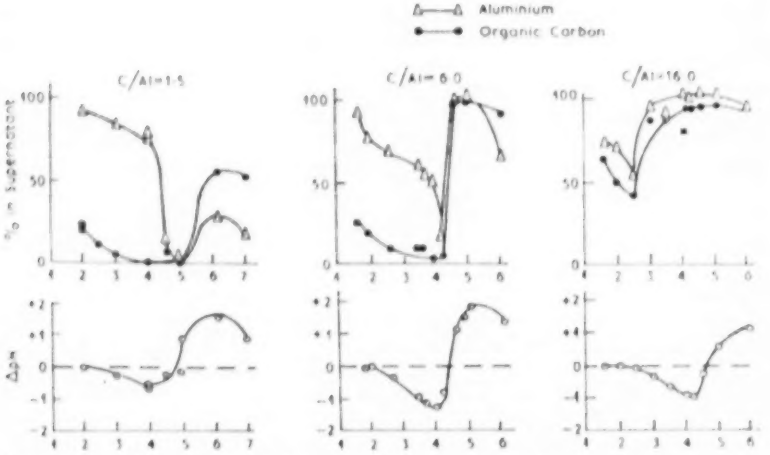

FIG. 1. Flocculation of Beerwah humus with aluminium, showing changes in pH on mixing. Mean pH of the two phases before mixing is given on abscissae of all curves.

Considerable amounts of free Al existed in suspension or solution at about pH 2, after which the Al concentration dropped rapidly with rise in pH to the precipitation point. Organic matter, although dispersed to some degree at pH 2, was flocculated relatively more completely. Thus the floc precipitated at low pH had a higher C/Al ratio than existed in the original mixture, which again agrees qualitatively with Mattson's results.

At pH values above the pH of maximum precipitation there was virtually complete dispersion of both Al and humus at C/Al ratios of 3 and over. The transition pH value dividing complete flocculation from complete dispersion was very sharp and was found to occur over a maximum pH range of 0·1 unit. For example, in the series C/Al = 6, complete flocculation was observed at pH 4·27 whereas both constituents were completely dispersed at pH 4·35. At C/Al = 1·5 in Fig. 1 there was a tendency for partial flocculation of both constituents at pH values greater than 5·0 although on the acid side of this value the general situation was similar to the other series. At C/Al ratios of $< 1{\cdot}5$ it is probable that mutual flocculation would occur over a greater pH range, but in view of the higher value of the C/Al ratio found in the humus portion dispersed with acetylacetone (Martin and Reeve, 1957*b*) this was not investigated.

The flocculation of Te Kopuru humus at C/Al = 2·75 and 6·0, and of Woolnorth humus at C/Al = 6·0, was also investigated. Essentially similar results were obtained except that the humus from the New Zealand podzol appeared less sensitive to flocculation even at a C/Al ratio lower than that existing in the B horizon in the original soil. However, as with the Beerwah humus, maximum precipitation took place in the same narrow range (pH 4–5).

Some insight into the nature of the ionic species causing flocculation may be inferred from the change in pH observed on mixing the two phases. The actual pH drift which took place on diluting either humus or metal salt with an equal volume of water, was found to be always positive, i.e. a rise in pH occurred, which was expected and varied from +0·09 to +0·29 units. However, owing to the uncertainties involved no correction has been made in the pH differences (ΔpH) recorded in the humus–metal ion systems, but the errors are not believed to alter the general conclusions.

The lower curves in Fig. 1 give plots of ΔpH against mean pH of the two phases before mixing. At all C/Al ratios, including that at 16·0 where peptization was observed over pH 2·6, ΔpH attained a maximum negative value at pH 4·0. It then became zero at pH 4·2–4·8 and thereafter assumed a large positive value which often approached 2 pH units. Even at a C/Al ratio of 24·0 (not shown in Fig. 1) where dispersion was complete at all pH values from 1·8 to 5·0, these alterations in sign of ΔpH were observed at precisely the same mean pH levels. At C/Al ratios of 6·0 and less, the zero value for ΔpH exactly coincided with the point of maximum precipitation of both constituents. A plot of ΔpH on mean pH for all Al-humus systems studied (including a 'humic acid' preparation isolated from the Waco Clay) is given in Fig. 2. The freehand curve drawn fits all points fairly closely, suggesting the operation of a general law with these systems.

Brosset (1952), in a study of the different ionic species formed during the hydrolysis of aluminium salt solutions, postulated that as the pH of such solutions was raised, successive dimerization of the Al-hydroxo-complexes occurred, accompanied by a decrease in the nett charge per Al atom. The reactions were considered to take place according to the following scheme:

$$Al^{3+} + Al^{3+} + 3H_2O \rightarrow Al_2(OH)_3^{3+} + 3H^+ \qquad \text{(i)}$$

$$Al_2(OH)_3^{3+} + Al^{3+} + 3H_2O \rightarrow Al_3(OH)_6^{3+} + 3H^+ \qquad \text{(ii)}$$

or more generally

$$Al_{(n-1)}(OH)_{3(n-2)}^{3+} + Al^{3+} + 3H_2O \rightarrow Al_n(OH)_{3(n-1)}^{3+} + 3H^+ \qquad \text{(iii)}$$

On the basis of his results Brosset listed a table relating pH and $\bar{n}$ (the average number of OH-groups per atom of Al) for the system $Al^{3+}nH_2O$ at 40°C. (this temperature was chosen to ensure rapid attainment of equilibrium). A curve plotting this relation at an Al concentration of $2{\cdot}209 \times 10^{-3}$ molar is shown in Fig. 3. From this the average 'valency' of the Al atom ($= 3 - \bar{n}$) was interpolated and the results

applied to several flocculated Al-humus systems described above. These systems were selected as they were nearly equal in Al concentration (2·7 mg. Al in 40 ml. or $2{\cdot}5 \times 10^{-3}$ molar) to one system described in Fig. 3. This is important as Brosset showed that $\bar{n}$ increases considerably with increasing concentration of Al at the same pH value. Assuming that all the Al which flocculated the humus between pH 2 and pH 4·5 (see Fig. 1) had replaced exchangeable hydrogen ions on the surfaces

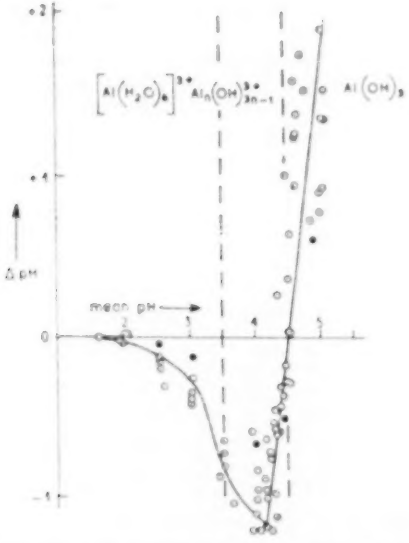

FIG. 2. Relation between mean pH of Al and humus phases before mixing, and change in pH 24 hours after mixing. (Black circles = Waco 'humic acid', others humus from podzols.)

of the humus particles, that the unflocculated Al was present as free Al ions and, finally, taking into account the change in nett charge of the Al ions as the pH value approaches 4·5, the theoretical change in pH on mixing could be calculated. Fig. 4 shows comparisons between the theoretical and actual curves so obtained on three different Al-humus systems. Close agreement was obtained except that the pH drop found was generally less than that calculated, especially at higher pH. This is thought to be due to two factors:

(i) As NaOH was used to raise the initial pH of the organic matter suspension the proportion of exchangeable hydrogen decreased with rise in pH.

(ii) At pH values at and above 4·0, release of hydroxyl ions from the surface of the aluminium hydroxide polymers occurred (this will be discussed fully below) and the actual pH recorded was the resultant of the release of both H_3O^+ and OH^-.

The close agreement between the calculated and observed values suggests that reactions similar to those postulated by Brosset can occur

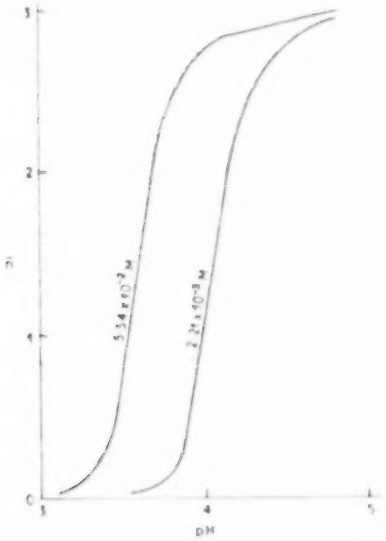

FIG. 3. Relation between pH and $\bar{n}$ (average number of OH per atom of Al) for the system Al^{3+},nH_2O at 40° C. at two concentrations of Al (after Brosset).

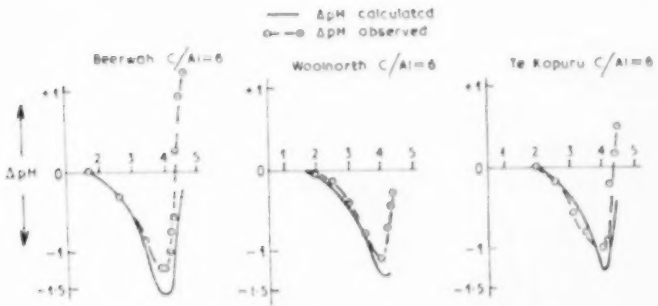

FIG. 4. pH differences (calculated and observed) on mixing Al and humus suspensions at increasing pH values (abscissae indicate mean pH of Al and humus phases).

and leads to the conclusion that maximal precipitation of both Al and humus at pH 4·0–5·0 and at C/Al ratios less than 12·0 is probably facilitated by polymeric forms of Al hydrous oxide containing a number

of positively charged spots. The product of equation (ii), for example, can probably take the form:

which suggests that a highly efficient bridging could be formed with adjacent negative positions on the humus particles. A similar situation exists sterically with respect to the aggregating properties of soil conditioners except that in this case negatively-charged polymer chains are thought to be implicated.

One difficulty that has not yet been resolved is that polymerization might be expected to reverse at pH 4·0 by reason of the large pH drop (ΔpH = approx. 1·0) caused at this acidity. The final mixing pH has not been observed to alter at least for several days after mixing. In the absence of any positive evidence on this point it is suggested that, once formed, the Al hydrous oxide polymers are considerably stable. Martin and Reeve (1958) reported hysteresis effects on forward- and back-titration of Al-containing humus preparations which were thought due to the slowness with which freshly precipitated Al-'hydroxide' attains equilibrium on adding acid.

At pH values above the point of maximum precipitation the rise in pH can be explained by the release of hydroxyl ions from the surface of the precipitated hydrous oxide by 'humate' anions. At this pH the humus fraction (pK_a = approx. 4·0) was more than half-neutralized so that considerable amounts of these anions were present. Of special interest in this connexion are the review papers by Pokras (1956 *a*, *b*, and *c*); in particular the rise in pH caused by adding various anions to colloidal Al hydrosols (Pokras, 1956*a*). The effects of various inorganic anions in blocking the anion-exchange groups on Al-'hydroxide' and thus preventing exchange with humus anions were tested (following Pokras) as follows: five separate aliquots of a solution of $AlCl_3$, each containing 2·5 mg. Al in 10 ml., were each adjusted to pH 4·78 with alkali, giving an opalescent sol which did not appear flocculated. Separate 1 ml. portions of 0·05 N solutions of the sodium salts of various anions (see Table 1) were then added and the pH change recorded. The expected order of pH rise (ΔpH (1), Table 1) was followed; oxalate released most OH^-, halides least. The pH of each system was then adjusted to approximately its original value by addition of acid. Separate 5 ml. aliquots of a suspension of Beerwah humus were then added to each tube and thoroughly mixed. After overnight standing the pH values were rechecked. Table 1 shows that the halide systems gave the largest OH^- release, whereas the added sulphate and oxalate partly occupied the exchange sites previously held by OH^- preventing maximal release of hydroxyl. In contrast to the results of Thomas and Whitehead quoted by Pokras (1956*a*), sulphate was more efficient in this respect

than oxalate; however, true equilibrium pH conditions were difficult to achieve in the systems containing sulphate and oxalate since they flocculated immediately on adding the sodium salt.

TABLE 1

Release of Hydroxyl by 'Humate' following Treatment with Different Anions

Initial pH *of* $AlCl_3$ *solution*	*Anion added* ml. 0·05 N	pH (*immediate*)	ΔpH(1)	pH *adjusted to*	mg. C *added*	pH *of* C *preparation*	*New* pH (20 *hrs.*)	ΔpH(2)†
4·78	1 ml. oxalate	7·33•	+2·55	4·84	15·8	4·78	5·77•	+0·96
4·78	1 ml. sulphate	5·91•	+1·13	4·70	15·8	4·78	5·22•	+0·48
4·78	1 ml. iodide	4·80	+0·02	4·75	15·8	4·78	6·27•	+1·51
4·78	1 ml. chloride	4·81	+0·03	4·74	15·8	4·78	6·28•	+1·52
4·78	1 ml. H_2O	4·79	+0·01	4·72	15·8	4·78	6·32•	+1·57

• pH values not at equilibrium and rising slowly.
† Calculated from the mean of columns 5 and 7.

The peptizing action of humus above pH 4·5–5·0 must therefore be accompanied by anion exchange, part or whole of the humus anion combining chemically with the surface of the 'hydroxide' by replacement of OH^-. That this is probably a general property of humus from sources other than podzol B horizons is shown in Fig. 2, where the black clay 'humic acid' extract also showed marked pH rises above pH 4·5. It is of interest in this connexion that Leaver and Russell (1957) showed that metal-free sols of 'fulvic acid' (prepared with 'Amberlite' IR/120) are effective in blocking sorption of phosphate by soils. They suggest however that this is not due to a specific chemical blocking but is a physico-chemical phenomenon in which replacement of OH^- by dissociated organic acids gives rise to a negative surface on the soil particles which repels $H_2PO_4^-$ ions.

At a C/Al ratio of 1·5 it is apparent that at pH 6–7 both constituents co-precipitated to some extent and that, concurrently, ΔpH values were smaller than in the other series and decreased with increase in alkalinity. This is attributed to the formation of a more crystalline hydrous oxide with a lower surface area and lower capacity for anion exchange, which precipitated and carried down with it some adsorbed organic matter. There is some evidence of this effect at C/Al ratios of 3 and 6 (see Fig. 1) at pH 6, but as the C/Al ratio widened the deflocculating action of humus became increasingly efficient.

Sorption of humus by H- and Al-clay. Fig. 5 shows that sorption of humus by Al-bentonite was virtually complete at pH 2 and 3, but decreased steadily with rise in pH; at pH 6 less than half the added humus was sorbed. It is also clear from Fig. 5 that some of the Al was present as free ions at low pH, despite the fact that symmetry amounts were added to the clay, and it is probable that a portion of the humus fraction was flocculated by Al ions, as well as sorbed by Al-clay, at pH 2. Sorption of humus by H-saturated bentonite was appreciable only at pH 2; above this value, sorption was slight or negligible, in direct contrast to Al-bentonite.

Changes in pH on mixing the bentonite and humus systems were complicated by the fact that equilibrium pH conditions were difficult to attain in the clay systems before mixing. Even after 24 hours equilibration at 25°C., both H- and Al-bentonites (in absence of humus) were showing slight decreases of pH with time. The ΔpH values shown in the lower portion of Fig. 5 are consequently unreliable, but it is seen that

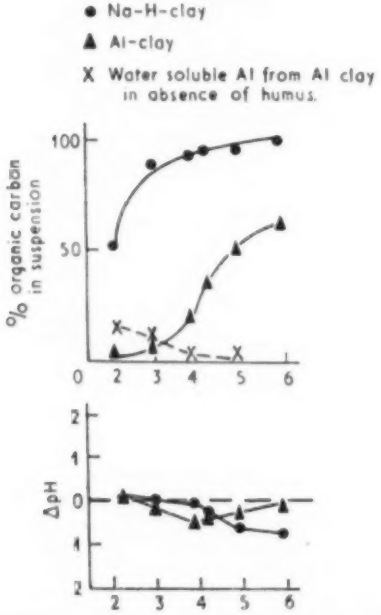

FIG. 5. Sorption of Beerwah humus by Al-bentonite and Na-H-bentonite. (Abscissae indicate mean pH values of clay and humus before mixing.)

for Al-bentonite, the decrease in pH on mixing attains a maximum at pH 4 and then becomes smaller with rise in mean pH, suggesting that the formation of Al hydrous oxide polymers has not been wholly inhibited by the fact that Al is present in exchangeable form. Values for ΔpH did not become positive in the presence of clay as occurred in its absence, so that it is not possible to argue positively that humus sorption at pH 5 and 6 was facilitated by exchange with hydroxyl. It is probable that clay buffering properties masked a precise interpretation of the results from considerations of the changes in pH on mixing.

Both H- and Al-bentonite self-flocculated strongly, but addition of humus caused some degree of dispersion in both cases at all pH values. The dispersing effect was more marked with the H- and Na-H-clay but the Al-clay was also moderately dispersed at all pH values. These properties were also noted with H- and Al-kaolinite. Bloomfield (1957)

noticed similar effects on kaolinite with aqueous plant extracts at pH 3·0, which may be caused in both cases by blocking of positive charges (Schofield and Samson, 1954) on the edges of the clay crystals by sorption of humus.

Acknowledgement

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REFERENCES

Aarnio, B. 1913. Int. Mitt. Bodenk. **3,** 131.
Bloomfield, C. 1957. J. Sci. Food Agric. **8,** 389.
Brosset, C. 1952. Acta Chem. Scand. **6,** 910.
Deb, B. C. 1949. J. Soil Sci. **1,** 112.
Dion, H. G. 1944. Soil Sci. **58,** 411.
Harward, M. E., and Coleman, N. T. 1954. Ibid. **78,** 181.
Leaver, J. P., and Russell, E. W. 1957. J. Soil Sci. **8,** 113.
Martin, A. E., and Reeve, R. 1957*a*. Ibid. **8,** 268.
—— —— 1957*b*. Ibid. **8,** 279.
—— —— 1958. Ibid. **9,** 89.
Mattson, S. 1931. Soil Sci. **31,** 57.
Paver, H., and Marshall, C. E. 1934. J. Soc. Chem. Ind. **12,** 750.
Pokras, L. 1956*a*. J. Chem. Educ. **33,** 152.
—— 1956*b*. Ibid. **33,** 223.
—— 1956*c*. Ibid. **33,** 282.
Schofield, R. K., and Samson, H. R. 1954. Disc. Faraday Soc. **18,** 135.

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CHEMICAL STUDIES OF PODZOLIC ILLUVIAL HORIZONS

V. FLOCCULATION OF HUMUS BY FERRIC AND FERROUS IRON AND BY NICKEL

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Summary

Resin-treated humus extracts, adjusted to predetermined pH values, were mixed with solutions of $FeCl_3$, $FeCl_2$, or $NiCl_2$ at the same pH. At C/Fe(III) ratios of 3 and 6, maximum precipitation of humus and Fe occurred at pH 2–3, i.e. the approximate precipitation pH of hydrous ferric oxide. Above pH 3, humus was almost completely dispersed; Fe was partially precipitated at pH 5 without extensive co-precipitation of humus. At ratios of C to Fe(III) found in the B horizon of a New Zealand podzol (C/Fe(III) = 22), no flocculation of humus occurred at any pH value from 1 to 5. Using $FeCl_3$ and $AlCl_3$ as a mixed flocculant (C/Al = 12, C/Fe(III) = 5·8) complete flocculation of humus occurred from pH 1·8 to pH 4. Comparison of the results with data from pure Al and Fe systems suggested that Fe was the active precipitant at pH 3 while Al was active from pH 3 to pH 4.

Flocculation of humus by Fe(II) was complete at pH 6–7, but only at C/Fe(II) = 1. At C/Fe(II) = 2 flocculation was partial, the maximum occurring at pH 5. As with the ferric systems, maximal flocculation appears to occur at about the precipitation pH of the metal 'hydroxide'. Nickel (C/Ni = 3) did not flocculate humus at any pH from 1 to 8. Thus greater amounts of divalent ions are needed to flocculate humus, in agreement with the Hardy-Schulze effect.

Experiments testing the effect of atmospheric oxidation of ferrous-humus systems on flocculation were, in general, inconclusive, although slight precipitation of humus was observed following aeration of a ferrous-humus system at pH 3.

Changes in pH occurred on mixing humus with all metal solutions studied, whether flocculation occurred or not. These changes were negative below a critical mixing pH which depended on the metal species used, and positive above this value. The critical pH values for Fe(III), Fe(II), and Ni were 2·8, 6·8–7·8 (depending on reaction time), and 8·0 respectively; for a mixed Fe(III)–Al system the critical pH was 4·2. An interpretation of these changes is suggested in the case of ferric iron, that is based on that previously postulated for Al.

Semi-quantitative experiments showed that Ni, Fe(II), and Al ions possess additive properties in flocculation of podzol humus at pH 2·96. Organic matter which contained slightly less than the critical amount of Al necessary for flocculation was still dispersed but highly sensitive towards the addition of small amounts of Fe(II) or Ni which by themselves were without effect. Freshly precipitated hydrous ferric oxide did not sensitize humus towards flocculation by Al at pH 3·2, although considerable amounts of Fe(III) could be co-precipitated by adding Al in excess of the critical concentration.

Introduction

THE ratio of atomic weights of Fe and Al is 56/27 or approximately 2. An organic carbon/Al ratio of 6·0 is therefore equivalent, on a basis of equal molarity, to an organic carbon/Fe ratio of about 3. The ratio of C to Fe extractable by acetylacetone (both as Fe-acetylacetone complex

and as dispersed but uncomplexed Fe) exceeded 20 in the case of the Beerwah and Te Kopuru podzol B horizons (Martin and Reeve, 1957) and greatly exceeded this value in the Woolnorth podzol. Thus it appeared likely, from a consideration of the results of the Al-humus systems presented in the previous paper of this series (Martin and Reeve, 1959*a*), that mutual flocculation would not occur at C/Fe ratios of 20. In Part II of this series (Martin and Reeve, 1957) it was suggested that Fe played little or no part in the precipitation of humus in the B horizon of the Te Kopuru soil. Many podzols are found, however, in

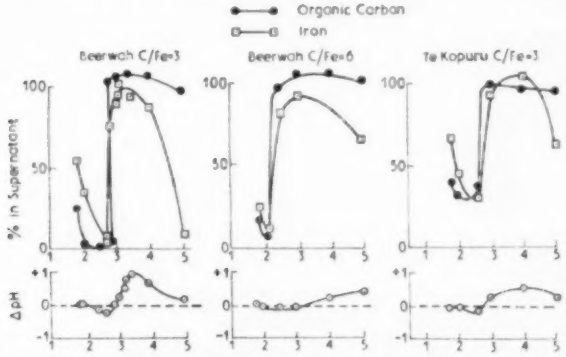

FIG. 1. Flocculation of podzol humus with ferric iron at increasing mean pH values of each phase (abscissae) showing changes in pH on mixing.

which the amounts of illuvial iron are roughly equal to those of aluminium and it was, therefore, of fundamental interest to study the flocculating properties of Fe, at a similar molar concentration to that of Al, to compare the flocculating action of these two metals.

Flocculation by Iron(III)

Experimental. Humus suspensions were prepared from the Beerwah, Te Kopuru, and Woolnorth podzols and purified by centrifuging and freed as far as possible from entrained Al by resin treatment. Twenty ml. aliquots of humus suspension containing generally 16–17 mg. organic C were adjusted to predetermined pH values and mixed with an equal volume of a solution of A.R. ferric chloride, containing 2–5·5 mg. Fe^{+++}, at approximately the same pH (±0·03 pH). After allowing 24 hours to reach equilibrium, the supernatant liquid was analysed for organic carbon (Walkley and Black titration). Following perchloric acid digestion, total Fe was determined on a portion of the diluted digest using *o*-phenanthroline in the presence of hydroquinone.

Results. Fig. 1 indicates the flocculating properties of Fe on Beerwah and Te Kopuru humus. There were general similarities to the Al-humus systems except that the pH of maximum precipitation of both constituents varied between 2 and 3 according to C/Fe ratio, i.e. approximately at the pH of precipitation of ferric 'hydroxide'. At mean pH

values above that for 'hydroxide' precipitation the humus phase was completely dispersed, as in the Al series; but the Fe concentration fell sharply following an initial maximum which was in some contrast to the behaviour of Al except at low C/Al ratios. Unlike Al, however, the precipitated hydrous ferric oxide did not show marked co-precipitation of organic matter.

The Te Kopuru humus at C/Fe = 3 was more dispersed even at the maximum flocculation point but the general features of the pH-flocculation curve were preserved. Woolnorth humus (for which results are

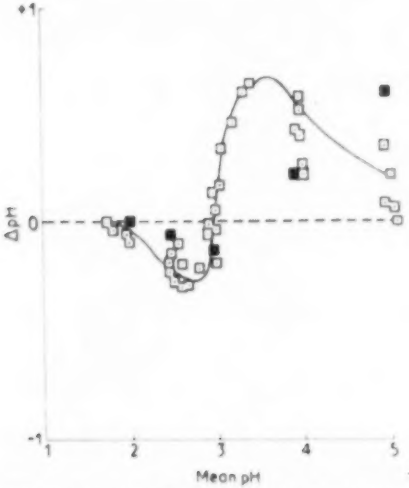

FIG. 2. Relation between the mean pH of Fe(III) and humus phases, and change in pH 24 hours after mixing (ΔpH) (Black squares = Waco 'humic acid').

not shown here) showed similar flocculating properties towards Fe as did the Beerwah preparation.

At a C/Fe ratio of 22 (the ratio existing in the B horizon) Te Kopuru humus was completely dispersed at pH 1–5, agreeing qualitatively with the experience with Al-humus systems with a wide C/Al ratio.

The lower portions of Fig. 1 illustrate the relation between ΔpH and the mean pH value of the two phases before mixing. A lowering of pH occurred between pH 1·6 and 2·8 (with a maximum at about pH 2·0); ΔpH reached zero values at pH 2·8–3·0 and became increasingly positive thereafter, attaining maximum positive value at pH 3·5–4·0. Fig. 2 shows the relation between ΔpH and mean pH from all experiments (including 'humic acid' from a neutral Queensland black earth) and, as with Al, it seems that a general relationship exists. The mechanism controlling these pH changes may, therefore, be similar to those suggested for Al: displacement of exchangeable hydrogen from humus by Fe^{+++} at low pH, anion exchange of surface OH^- by 'humate' at pH

3·0 and over, and an intermediate stage where, perhaps, ferric 'hydroxide' dimers are present in the system which cause maximum precipitation of organic matter. There is evidence from the literature for polymerization of ferric 'hydroxide'. Milburn and Vosburgh (1955) and Mulay and Selwood (1955) postulate the formation of a dimer. The latter authors (loc. cit.) calculate that at pH 2·5 in 0·4 M solution

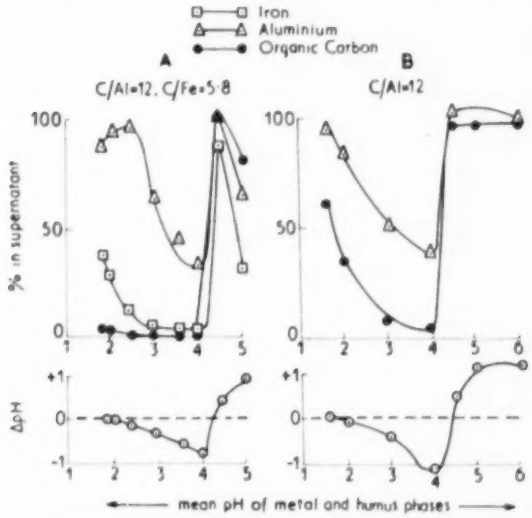

FIG. 3. Flocculation of Beerwah humus and Al in presence (A) and absence (B) of Fe(III), showing changes in pH on mixing.

the proportion of Fe dimers accounts for about 60 per cent. of the total Fe present, with $Fe(OH)^{++}$ accounting for 10 per cent. and $Fe(OH)_2^+$ for about 2·5 per cent.

The fall in pH following the maximum value at pH 3·5–4·0 was probably due, as for Al in the previous paper, to a lowering of surface area of the freshly precipitated 'hydroxide' at progressively higher pH values. Numerically, ΔpH was not as high for Fe as for Al on the alkaline side of pH 3·0. This may have been due to a lower concentration of humus anions at pH 3·0 at which Beerwah humus was about 20 per cent. dissociated as against 57 per cent. dissociated at pH 4·5 (see Fig. 1, Martin and Reeve, 1958). On the other hand an 'intensity' factor is of course also involved; a pH value of 1 unit represents a hundredfold increase in OH^- release at pH 3·0 compared with pH 5·0.

Flocculation by a Mixed Aluminium-Iron(III) System

If, as is generally accepted, podzolization is characterized by a fall in soil pH with time, the previous results on flocculation of humus by Al and Fe theoretically suggest that humus will be completely flocculated at pH 4–5, i.e. in a pH region where Fe has no precipitating action on

humus at all. The flocculation of Beerwah humus by a mixed preparation of aluminium and iron(III) chlorides was next studied in an attempt to test this hypothesis.

Results. The ratio of Fe to Al used was such that the C/Al ratio of the final mixture was 12·0 and the C/Fe ratio 5·8. The results are illustrated in Fig. 3A. Comparison with Fig. 3B (flocculation by Al alone at C/Al = 12·0) shows that from pH 1·8 to pH 4·0 similar amounts of Al remained in the supernatant in presence or absence of Fe, whereas Fe almost completely precipitated from pH 3·0 to pH 4·0 (where in absence of Al it resulted in some dispersion, see Fig. 1). Organic matter precipitation was virtually complete up to pH 4.0 and clearly Fe^{+++} and, at higher pH, Al ions were operating as flocculating ions in this range. At pH 4·4 there was a transitory dispersion of all components (as for Al alone at this pH) but at pH 5 both Al and Fe hydrous oxides precipitated, bringing down also some humus. The ΔpH values were identical with those found for Al separately; there was no rise at pH 3 or over (precipitation of Fe) and it was assumed either that this did not occur in the mixed system or that, if it did, it was masked by the larger negative value for ΔpH caused by Al. Co-precipitation of Fe certainly occurred at pH 3·0–4·0; hence a Fe-Al-humus precipitate could theoretically be obtained which had been flocculated only by Al. This effect was further tested and the results are reported later in this paper.

Flocculation by Iron(II)

Reduction of iron compounds to the ferrous state in soils has been repeatedly postulated for a number of pedogenic processes, particularly podzolization (Schnitzer and DeLong, 1952; Bloomfield, 1953) and gley formation (Hénin and Bétrémieux, 1948; Bloomfield, 1950, 1951). Normally, ferrous ions are readily susceptible to atmospheric oxidation and these workers have suggested that complex-formation stabilizes iron in the reduced state. Whether this is correct or not (and there are theoretical reasons against such a hypothesis which will be reviewed in a later contribution), it is clear from results presented previously (Martin and Reeve, 1958) that ferrous ions would not form such complexes with B horizon organic matter. However, the flocculating properties of ferrous ions with respect to humus were considered of sufficient importance to study experimentally. In particular, it was desirable to confirm whether or not the known differences between ferrous and ferric ions would be reflected in their mutual behaviour towards organic matter, in the light of the previous results for Al and Fe(III). For example, ferrous 'hydroxide' precipitates at a much higher pH value; the difference in valency suggests a lower flocculating power for ferrous ions; and some evidence of the behaviour of a ferrous-organic system towards atmospheric oxidation was required.

Experimental. A solution of analytical grade ferrous sulphate was prepared in distilled water that had been previously boiled, cooled, and saturated with pure hydrogen gas from a Tucker generator. In the flocculation tubes, the pH values of humus and ferrous ion phases were

adjusted to the desired value in a stream of hydrogen from the same source, to minimize oxidation. Beerwah humus was exclusively used in these experiments.

In a preliminary trial, using a C/Fe(II) ratio of 3.0, no mutual flocculation occurred over the pH range 2–7 (cf. the flocculation by Fe(III), Fig. 1). This was attributed to the operation of the Hardy-Schulze rule governing the quantitative effects of ion valency on the flocculation of colloids. Nevertheless, some exchange of Fe(II) with hydrogen on the organic matter took place since pH values decreased on mixing the two phases as for Fe(III) and Al, the maximum fall of 1·65 units being observed when the mean pH of the two phases reached 5·4. To test the effect of oxidation of Fe(II) to Fe(III) (the latter being the more powerful flocculant) oxygen was passed through all the systems after 24 hours. There were tentative indications that partial flocculation occurred in some treatments, which had a final pH on mixing of 3·4 or less. As such oxidation could cause complications in the interpretation of the results and since the quantitive effects of this type of oxidation were important, a method of determining free ferrous ions in the presence of organic matter was devised.

Determination of Fe(II) in presence of organic matter. Five ml. aliquots of humus suspensions containing ferrous ions were transferred to beakers; 3 ml. A.R. syrupy phosphoric acid and 25 ml. 2 N HCl were added to each and the total volume adjusted to 50 ml. Each beaker was placed in a Fisher titrimeter (fitted with a bright platinum electrode and saturated calomel electrode as reference cell) and small additions of 0·01 N potassium dichromate made with automatic stirring. The redox E.M.F. was noted after each addition of oxidant and the end-point of the titration determined by interpolation at the point of inflexion of the E.M.F.-titration curve. Preliminary tests showed quantitative recovery of Fe(II) in presence of widely varying amounts of organic matter from the Beerwah profile (0–19 mg. C). Furthermore, the presence of humus did not alter the position of the E.M.F. at the end-point; thus no interfering reducing compounds were present in this humus fraction at the high acidity employed.

In succeeding experiments, aliquots of the supernatant liquid from each tube were analysed for Fe(II) as described above and for total Fe by *o*-phenanthroline after perchloric acid digestion. Iron (III) was calculated by difference.

Results. Fig. 4A illustrates the pH-flocculation characteristics of a system containing organic carbon and Fe(II) at a ratio of 1·0. In contrast to the 3·0 ratio, considerable flocculation of humus was observed at all pH values from 2 to 7·8. Ferrous iron concentration diminished continuously as pH increased; total Fe closely followed the same pattern except for a sharp rise at pH 7·8 suggesting that partial oxidation at this pH formed a humus-protected iron sol. The values for ΔpH again indicate exchange reactions of the type previously described. A transitory positive value was recorded at pH 8 which became negative after standing overnight. Thus the fresh ferrous 'hydroxide' precipitate appears to possess anion-exchange properties towards humus; subsequent oxidation

reduces the hydroxyl ion concentration, probably by a reaction similar to the following:

$$Fe(OH)_2 \longrightarrow Fe(OH)_2^+ + e$$

$$Fe(OH)_2^+ + OH^- \longrightarrow Fe(OH)_3$$

A fall in pH was also recorded by Hemstock and Low (1953) during the oxidation of manganous ions in clay systems. Even though atmospheric oxidation was avoided as far as possible some oxidation of ferrous ions could not be prevented. The results of Gayer and Woontner (1957) suggest that the strong reducing properties of freshly precipitated

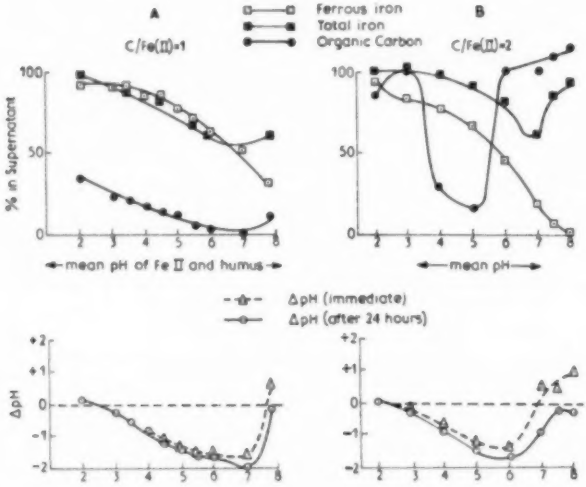

FIG. 4. Flocculation of Beerwah humus by Fe(II) showing changes in Fe(II) concentration and pH on mixing.

ferrous hydroxide effect the reduction of water (which is presumably reduced to hydrogen) and this type of reaction may have occurred in the systems described here, possibly before mixing with the humus phase.

It is clear from Fig. 4A that maximal precipitation of humus occurred at pH 7·0. Pure ferrous 'hydroxide' gives a white gelatinous precipitate at pH 8·1, but only in the complete absence of air and ferric ions (Arden, 1950). The green precipitate formed at lower pH values is probably ferrosic hydroxide formed by the reaction of ferrous ions with ferric 'hydroxide'—

$$2Fe(OH)_3 + Fe^{++} + 2OH^- \longrightarrow Fe_3(OH)_8$$

As the $FeSO_4$ solution employed in these experiments contained a small amount of ferric iron the lowered pH of maximum precipitation shown in Fig. 4A can be accounted for. Bloomfield (1955) commented on the adsorption of ferrous ions by hydrous ferric oxide and it is probable

that a series of 'ferrosic hydroxides' can be formed, depending on the ratio of Fe(II) to Fe(III) in the system. Since, as discussed above, some oxidation of $Fe(OH)_2$ can also occur by reduction of water, the actual hydrous oxide precipitated would be the resultant of a number of uncontrollable factors. It is however apparent that, whatever its final composition, ferrous 'hydroxide' exhibited the same general flocculating properties towards humus except as regards concentration, as did its Al and Fe(III) analogues.

By contrast, at C/Fe = 2·0 (Fig. 4B) the flocculation of humus was incomplete and occurred within the comparatively narrow pH range of 4·0–5·0. Ferrous iron diminished continuously in concentration from pH 2·0 to pH 8·0 (at pH 7·5 and 8·0 there was evidence of oxidation of ferrous iron as in the previous series) but at all recorded pH values total Fe concentration exceeded that of Fe(II) indicating more extensive oxidation than before. The minimum ΔpH value was recorded at pH 6·0 for C/Fe(II) = 2·0 but at C/Fe(II) = 1·0 this value occurred at pH 7·0.

It is difficult to explain the increased oxidation of Fe(II) at C/Fe = 2·0, compared with C/Fe = 1·0 where significant oxidation occurred only at pH 7·8. A final experiment was conducted under conditions in which atmospheric oxidation was, at least in theory, reduced to negligible proportions. The separate humus and ferrous systems were placed in two limbs of a Y-shaped tube. The pH value and volume of each was adjusted to the same value; during this operation, and for 10–15 minutes afterwards, pure hydrogen was passed continuously through each system. Both systems were mixed thoroughly by tilting the apparatus from side to side and the final suspension transferred (still under an atmosphere of hydrogen) to a U-tube. After bubbling hydrogen through the liquid for several minutes longer, the two ends of the U-tube were sealed with bungs and clamps. The liquid was sampled at roughly daily intervals (hydrogen was passed through the liquid at each sampling) and analysed for total and ferrous iron.

In spite of these precautions, oxidation of ferrous iron was observed during the first three days of the experiment, and the results are therefore inconclusive. It is clear that, either contamination by air occurred from an unsuspected source, or the oxidation of ferrous iron was facilitated by a particular type of electron-transfer mechanism in the Beerwah humus fraction. As with the first experiment, there were indications that partial flocculation took place following aeration at final pH values of about 3·0.

The results suggest, however, the virtual impossibility of stabilizing ferrous ions in combination with humus in soils. If ferrous ions are produced and it seems from Bloomfield's work and others that, under certain circumstances, they can be formed, their occurrence in the B horizon must be negligibly small. In any event, the oxidation of a ferrous-humus suspension much above pH 3·0 would be expected to result in a fully peptized suspension, from the observations reported for the ferric systems. Only at about pH 3·0, a value rarely encountered in soils, and at high concentrations of ferrous ions, would atmospheric

oxidation be expected to result in flocculation of humus by the ferric ions so formed.

Flocculation by Nickel

A preliminary investigation of the flocculating action of nickel ions on humus was undertaken to complete this stage of the work on pure metal ion species. Nickel does not occur frequently in soils except on nickeliferous parent materials (Crooke, 1956) and is not in itself of importance in podzolization. It was, on the other hand, of interest to use

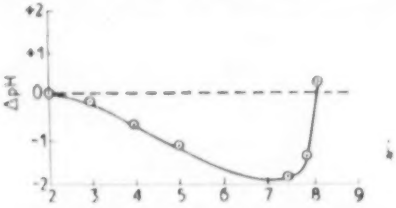

FIG. 5. pH differences found on mixing isohydric systems containing humus and nickel sulphate (C/Ni = 2).

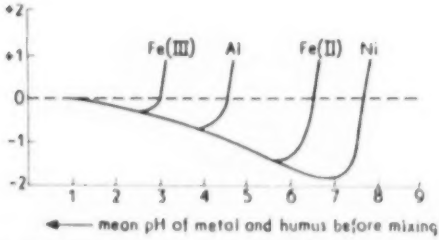

FIG. 6. Schematic representation of pH changes expected after mixing isohydric systems of metal ions and humus.

a divalent transition metal to confirm the operation of the Hardy-Schulze effect noted for Fe(II) and at the same time to ensure that the results were not in this case complicated by oxidation of the metal ions themselves, as had been found for Fe(II). The latter consideration ruled out cobalt and manganese.

One series of experiments only was performed, using solutions of nickel sulphate as flocculant, at a C/Ni ratio of 3·0. At pH values from 2·0 to pH 8·0, no flocculation was observed; very slight precipitation was, however, noted at the more alkaline pH's after 22 days. Changes in pH occurred on mixing, in conformity with previous experience for other metals; these changes are plotted in Fig. 5. The minimum ΔpH recorded occurred at a mean pH of 7·5 (Britton 1956, p. 62, reported incipient precipitation of the hydroxide at pH 6·7); at pH 8·2 a positive ΔpH was observed, indicating again the operation of exchange of surface hydroxyl for 'humate' anions. The fact that no flocculation took place at this ratio agrees with the results for ferrous iron at the same C/metal ratio in the previous series.

This experiment also provided an opportunity of rationalizing the ΔpH changes for all four metal species studied. Fig. 6 shows an idealized plot of the ΔpH values observed on mixing apparently isohydric preparations of humus and metal ions.

The four curves are sufficiently consistent to suggest that similar curves would be obtained by other cations which form insoluble metal 'hydroxides'.

The Additive Effect of Metal Ions in the Flocculation of Organic Matter

Experimental. The experiments described in this series were designed to answer two questions: (i) What were the minimal amounts of different types of metal ion needed to flocculate a given amount of humus?

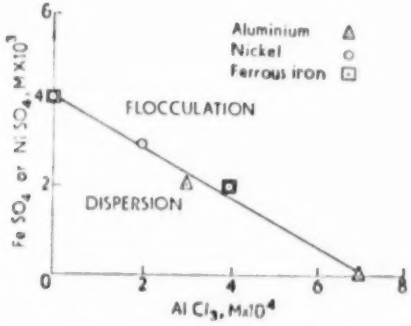

FIG. 7. Effect of concentration and valency of metal ion on flocculation of Beerwah humus.

(ii) Did the addition to organic matter of an amount of metal ion, less than the minimum required for flocculation, sensitize it towards further additions of the same (or another) metal and, if so, were these amounts additive?

An important consideration was to ensure that the observed flocculation effects were not complicated by changes in pH on mixing. All constituents were therefore present in a buffer medium which was a partially neutralized 0·1 N solution of formic acid, chosen since it does not form co-ordination complexes with metals.

To find the threshold concentration needed to flocculate Beerwah humus, 2 ml. purified suspension (containing 3·8 mg. organic carbon) was added to 8 ml. of formate buffer at pH 2·96 which contained known amounts of either nickel sulphate, ferrous sulphate, or aluminium chloride. To compare the flocculating action of two metals simultaneously, one of which was employed to pre-saturate partly the organic matter, volumes of formate buffer containing known amounts of (e.g.) Al were added to 2 ml. of the Beerwah preparation and thoroughly mixed. Measured amounts of (e.g.) Fe(II) or Ni solution in formate buffer, contained in separate tubes, were then mixed with the partly saturated

humus suspension. The final volume in both series was 10 ml. Flocculation effects were recorded qualitatively after overnight standing: the lowest concentration of metal at which precipitation occurred in each series was noted.

Results. The results are described by the linear relationship shown in Fig. 7. With pure Ni or Fe(II) systems, the lowest concentration of either metal at which flocculation occurred was 0·004 M. This was equivalent to a C/metal ratio of 1·70 for Fe(II) and 1·67 for Ni. Pure Al flocculated the humus at a minimum concentration of 0·0007 M corresponding to a threshold C/Al ratio of 20·1. These ratios were of the expected order in the light of previous results for Al and Fe(II) in this series; the C/Al ratio was, however, higher than expected, probably owing to the presence of buffer salts in the medium. The effect of preliminary additions of one metal caused a linear reduction in the amount of the other needed for flocculation as shown in Fig. 7.

A further experiment was performed to establish whether a humus sol, which had been treated with freshly precipitated ferric 'hydroxide', was sensitized towards flocculation by Al ions in the same manner. Using 0·1 N formate buffer at pH 3·2, graded amounts of Al solution in the same buffer were added to humus (3·8 mg. C) with and without added ferric 'hydroxide'. The lowest concentration of Al needed to flocculate the humus was the same in both series, although the actual value (0·0003 M) was much lower than in the previous experiment, possibly due to the difference in pH. This indicated that the hydrous oxide possessed no reinforcing effect on the threshold Al concentration at this pH. Furthermore, it was found by analysis of the supernatant liquid that considerable amounts of Fe had been removed from solution by co-precipitation.

These results have interesting consequences. A fully peptized Al-humus, containing only slightly less than the threshold amount of Al, would need, for example, quite small quantities of Fe(II) to flocculate it. In this hypothetical situation it is the ferrous ions which flocculate the system but there is clearly no doubt that Al, by virtue of its presence as a preliminary reinforcing ion, would be overwhelmingly involved in the final precipitation. Thus it may not be quite true to say, as was suggested from the results in Part II of this series, that Al was the 'active' precipitant (in the sense that it actually achieved the observed flocculation in the B horizon) in all cases; there is no reason, for example, why calcium or magnesium ions should not function this way. Deb (1949) found evidence for this using free Ca^{++}, but could not implicate exchangeable Ca^{++} in the precipitation process.

Moreover, it is apparent that co-precipitation of Fe, as humus-sorbed hydrous oxide, can also be induced by the flocculating action of Al ions, the threshold concentration of which was observed to be unaffected by the presence of Fe in this form. It may, therefore, happen that different sites on the humus micelles are responsible for sorbing (or being sorbed by) hydrous ferric oxide on the one hand, and active in bonding electrostatically with Al (causing flocculation) on the other.

REFERENCES

ARDEN, T. V. 1950. J. Chem. Soc. 882.
BLOOMFIELD, C. 1950. J. Soil Sci. **1**, 205.
—— 1951. Ibid. **2**, 196.
—— 1953. Ibid. **4**, 5.
—— 1955. Ibid. **6**, 284.
BRITTON, H. T. S. 1956. Hydrogen Ions, vol. ii. Chapman and Hall, London.
CROOKE, E. M. 1956. Soil Sci. **81**, 269.
DEB, B. C. 1949. J. Soil Sci. **1**, 112.
GAYER, K. H., and WOONTNER, L. 1957. J. Chem. Educ. **34**, 178.
HEMSTOCK, G. A., and LOW, P. F. 1953. Soil Sci. **76**, 331.
HÉNIN, S., and BÉTRÉMIEUX, R. 1948. C. R. Acad. Sci. Paris, **227**, 1393.
MARTIN, A. E., and REEVE, R. 1957. J. Soil Sci. **8**, 279.
—— —— 1958. Ibid. **9**, 89.
—— —— 1960. Ibid. **10**, 369.
MILBURN, R. M., and VOSBURGH, W. C. 1955. J. Amer. Chem. Soc. **77**, 1352.
MULAY, L. N., and SELWOOD, P. W. 1955. Ibid. **77**, 2693.
SCHNITZER, M., and DELONG, W. A. 1952. Sci. Agric. **32**, 680.

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DETERMINATION OF ORGANIC CARBON IN SOIL

I. OXIDATION BY DICHROMATE OF ORGANIC MATTER IN SOIL AND PLANT MATERIALS

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Summary

The organic carbon contents of a range of soils and of various organic materials (mostly of plant origin) were determined by the titrimetric methods of Tinsley and Walkley and Black, and the results compared with those obtained by Shaw's wet combustion method. Tinsley's method gave more reliable results with soils than Walkley and Black's method, but neither is satisfactory for precise work. Both give high results with organic materials less oxidized than elemental carbon and low results with organic materials more oxidized, although this effect is masked with materials which do not react completely under Walkley and Black conditions. Quantitative results were obtained on a range of whole plant materials with both Tinsley's and Walkley and Black's methods. The latter thus provides a very rapid method for the determination of carbon in plants. The carbon contents, determined by Tinsley's method, of a range of pure organic compounds agreed with the predicted values. Tinsley's method does not give quantitative results with certain soils, partly because of the oxidation level of the organic matter in these soils and partly because oxidation is incomplete.

Introduction

THE authors required a rapid method which was not affected by carbonate for determining organic carbon in small samples of soil. Titrimetric methods meet these requirements, but the results must be multiplied by an arbitrary correction factor to give results comparable to those by dry combustion. However, Tinsley (1950) described a titrimetric method which did not need a correction factor, but a full account of his method is not generally available. He determined the dichromate unused when a soil is heated under reflux with acid dichromate, and assumed that the dichromate used up was equivalent to the carbon in the sample, i.e. that the soil organic matter is at the same oxidation level as elemental carbon. Tinsley's method was compared here with Walkley and Black's (1934) method and with Shaw's (1959) method, in which the carbon dioxide evolved during acid-dichromate oxidation of soil organic matter is determined gravimetrically. Shaw standardized his method against dry combustion with excellent results which were confirmed by a number of dry combustions which we included in our work. Shaw's method was used as our standard throughout this work because it is more convenient than dry combustion.

Experimental

Materials

Soils. Table 1 describes the soils used. Samples 1, 4, and 7 were from the Broadbalk wheat plots at Rothamsted where the soil is derived from

Clay-with-Flints overlying Chalk. Sample 1 was from plot 7 ('complete minerals' and nitrogen annually), sample 4 from plot 3 (no manure or fertilizer since 1839), and sample 7 from plot 2B, having farmyard manure annually. Samples 2, 8, and 9 were brown earth soils from Anglesey (nos. 2 and 8: Castleton series; no. 9: Arvon series), sample 6 was from a gley soil profile in the same area (Cegin series). Sample 3 was from an old arable soil on the Upper Greensand, and sample 5 was a soil derived from Keuper Sandstone. Sample 10 was from a garden near Rothamsted which had been cultivated with heavy applications of organic manure for almost 100 years, and sample 11 was from a calcareous alluvial meadow soil (Broad series) under permanent grass near Reading, Berks. Samples 12 and 13 were from soils near Littleport (no. 12) and Swaffham (no. 13) in the Cambridgeshire fen district, sample 14 was from the surface of an Anglesey peat overlying a lacustrine deposit of calcium carbonate, and sample 15 was from an acid peat near Capel Curig. The samples were air-dried and ground to pass a 100-mesh sieve. In the analyses reported in Table 1, carbon was determined by Shaw's (1959) wet combustion method, nitrogen by a macro-Kjeldahl method which included nitrate and nitrite (Bremner and Shaw, 1958), pH by glass electrode, and $CaCO_3$ by Collins's (1906) method.

TABLE 1

Description of Soils

Sample no.	*Depth (in.)*	*Soil*	pH	*Percentage on moisture-free basis*		
				Organic-C	*Total*-N	$CaCO_3$
1	46–54	Clay	7·4	0·15	0·031	0·1
2	20–28	Sandy loam	5·9	0·16	0·034	0·0
3	0–6	Medium sandy loam	5·8	0·80	0·070	0·0
4	0–6	Clay loam	8·3	0·99	0·102	2·1
5	0–6	Fine sandy loam	6·5	1·77	0·161	0·1
6	13–20	Silty loam	4·8	2·15	0·175	0·0
7	0–6	Clay loam	8·0	2·56	0·250	2·4
8	0–6	Sandy loam	5·3	3·38	0·322	0·0
9	0–9	Sandy loam	6·3	4·18	0·375	0·1
10	0–6	Old garden	7·2	8·68	0·500	1·3
11	0–6	Clay loam	7·8	12·3	1·17	9·5
12	0–6	Fen	7·1	22·8	1·49	3·2
13	0–6	Fen	7·3	36·5	3·00	4·7
14	9–15	Low-moor peat	6·2	45·0	2·69	0·0
15	0–6	Mountain peat	3·7	53·6	2·07	0·0

Other materials. Glucose, sucrose, starch (soluble), oxalic acid, citric acid, tartaric acid, and urea were from Hopkin & Williams Ltd. (Analar grade chemicals); casein, edestin, chitin, sodium alginate, pectin (citrus), tannic acid, diphenylamine (Analar), resorcinol (Analar), pyrogallol (Analar), catechol, aspartic acid, glycine, and leucine from British Drug Houses Ltd.; cellulose (Whatman cellulose powder) from W. & R. Balston Ltd. The lignin preparations were commercial wood lignins sold under the trade names of Indulin A (lignin I) and Meadol MRM

(lignin II). The humic acid was a preparation isolated by acidification (pH 2·0) of an 0·5 M sodium-hydroxide extract of a mountain peat and subsequently purified by Forsyth's (1947) procedure. The compost was made by incubating straw with ammonium sulphate, and the lignoprotein preparation was isolated from a sodium-sulphite extract of this compost; the preparation and properties of these materials are described by Jenkinson and Tinsley (1959).

Methods

Dry combustion. Rickson's (1948) method was used: the carbon dioxide liberated by combustion of a sample containing 1–7 mg. of organic carbon was absorbed in baryta, and determined by titration with acid. Before analysis of calcareous soils the samples were pretreated in the combustion boat with a 5 per cent. (w/v) solution of SO_2 to remove inorganic carbon, and then dried *in vacuo* over KOH at room temperature (Bremner, 1949).

Wet combustion. Shaw's (1959) method was used: a sample containing 50–100 mg. of organic carbon was heated for 10 minutes with a mixture consisting of 4 g. of finely ground $K_2Cr_2O_7$ (Analar), 3 ml. of water, and 25 ml. of a 1·5:1 (v/v) mixture of concentrated H_2SO_4 and H_3PO_4 (sp. gr. 1·75), the CO_2 liberated being collected in soda-lime tubes and weighed. Before analysing calcareous soils, inorganic carbon in the sample was removed by treatment in the reaction flask with a 5 per cent. (w/v) solution of SO_2, the excess of this reagent being removed by evaporation *in vacuo* over KOH at room temperature. Attempts to determine organic carbon in calcareous soils by subtracting carbonate carbon from the total amount of carbon liberated as carbon dioxide on direct treatment of the soils with the chromic-sulphuric-phosphoric acid mixture used by Shaw were not successful, because the evolution of carbon dioxide from carbonates was not complete in the period of heating used in this method. This was probably due to the formation of a skin of calcium sulphate which protected some of the carbonate particles from the acid.

Tinsley method. The preliminary report published by Tinsley (1950) and personal communication with the author led to the adoption of the following procedure: an amount of sample estimated to contain about 10 mg. of organic carbon was weighed into a 500 ml. conical flask and treated with 25 ml. of 0·4 N $K_2Cr_2O_7$, 25 ml. of concentrated H_2SO_4, and 12·5 ml. of H_3PO_4 (sp. gr. 1·75). The flask was fitted with a 'cold finger' condenser and was boiled gently on a hot plate for 2 hours. The mixture was cooled, treated with 100 ml. of water, and residual dichromate was determined by titration with 0·2 N ferrous ammonium sulphate (prepared by dissolving 78·44 g. of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in 300 ml. of water containing 20 ml. of concentrated H_2SO_4 and diluting to 1 litre with water) using barium diphenylamine sulphonate solution (5 ml.) as indicator. This indicator solution, which was also used in the Walkley and Black method, was prepared by dissolving 0·3 g. of barium diphenylamine *p*-sulphonate and 58·7 g. of $BaCl_2.2H_2O$ (Analar) in 1 litre of warm water and filtering the cooled solution. The results were

calculated on the basis that 1 ml. of 0·4 N $K_2Cr_2O_7$ is consumed by 1·2 mg. of carbon.

Walkley and Black (1934) *method.* A slight modification of Walkley's (1935) method was used. An amount of sample estimated to contain about 10 mg. of organic carbon was weighed into a 500 ml. conical flask and treated with 10 ml. of N $K_2Cr_2O_7$ and 20 ml. of concentrated H_2SO_4, tha latter being added rapidly from a fast-delivery burette. The flask was immediately swirled vigorously for 1 minute, allowed to stand on a sheet of asbestos for 30 minutes, and treated with water (200 ml.) and H_3PO_4 (10 ml.; sp. gr. 1·75). The residual dichromate was determined by titration with N $FeSO_4$ solution (prepared by dissolving 278 g. of $FeSO_4.7H_2O$ (Analar) in 800 ml. of water containing 20 ml. of concentrated sulphuric acid and diluting to 1 litre with water) using barium diphenylamine sulphonate solution (5 ml.) as indicator. The results were calculated on the basis that 1 ml. of N $K_2Cr_2O_7$ is consumed by 3 mg. of carbon.

Results and Discussion

Table 2 gives the carbon content of the soils described in Table 1, as found by the methods listed above. Shaw (1959) showed that wet combustion, the reference method used in this work, gave results in close agreement with those of dry combustion and this is confirmed by the results in Table 2. The recovery of carbon by the Tinsley method

TABLE 2

Determination of Organic Carbon in Soils by Different Methods

	Method				
	Dry combustion	*Wet combustion**	*Tinsley†*	*Walkley and Black*	
				Actual	*Corrected‡*
Soil	*Organic carbon (percentage of air–dry soil)*				
1	..	0·150	0·145 (97)	0·085	0·110 (73)
2	..	0·160	0·169 (106)	0·105	0·136 (85)
3	0·80	0·80	0·75 (94)	0·63	0·92 (115)
4	..	0·98	0·90 (92)	0·71	0·88 (90)
5	1·80	1·76	1·70 (97)	1·40	1·84 (105)
6	..	2·09	2·19 (105)	1·82	2·40 (115)
7	2·53	2·52	2·51 (100)	2·10	2·77 (110)
8	..	3·30	3·29 (100)	2·53	3·34 (101)
9	..	4·09	3·61 (88)	3·30	4·35 (106)
10	..	8·45	8·20 (97)	5·23	6·80 (80)
11	11·3	11·4	11·2 (98)	9·7	12·6 (110)
12	20·6	20·8	18·3 (88)	17·3	22·5 (108)
13	..	30·6	28·8 (94)	25·3	32·8 (107)
14	..	38·1	33·1 (87)	31·3	40·7 (107)
15	..	47·2	47·8 (101)	43·5	56·4 (119)

* Method of Shaw (1959).

† Figures in parentheses are results expressed as percentages of wet combustion values.

‡ Actual × 1·30. Figures in parenthesis are results expressed as percentages of wet combustion values.

ranged from 87 to 106 per cent., averaging 96·3 per cent. The uncorrected Walkley and Black results were much lower; when the results were multiplied by the arbitrary correction factor (1·30) normally used with this method the average recovery of carbon was 102 per cent. However, the corrected recovery was more variable than by the Tinsley method, ranging from 73 to 119 per cent.

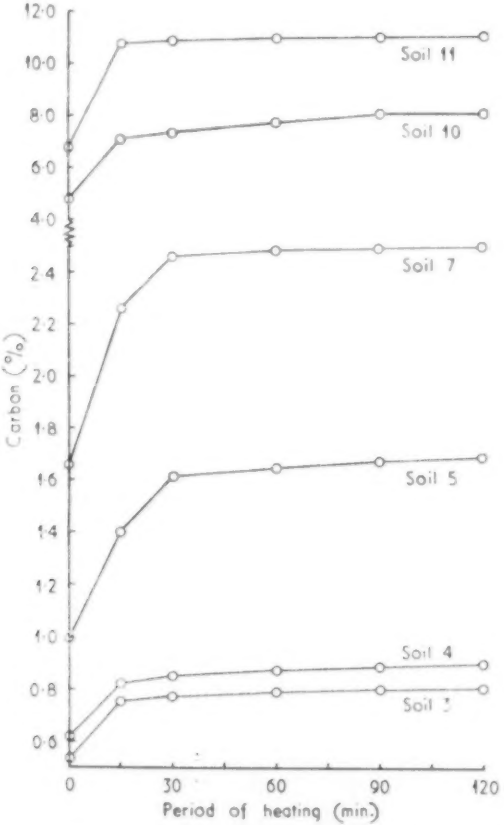

FIG. 1. Effect of varying period of heating in analysis of soils by the Tinsley method.

Fig. 1 shows the effect of varying the period of heating on the recovery of carbon from soils by the Tinsley method. Oxidation is rapid in the first 30 minutes but continues slowly thereafter, not being complete with some soils in 2 hours. The rate of oxidation of soil 10, which contains charcoal and possibly other carbonized material, is similar to that of the other soils which do not contain these materials.

TABLE 3

Determination of Carbon in Different Materials by the Shaw, Tinsley, and Walkley and Black Methods

Material	Method		
	Shaw	*Tinsley*	*Walkley and Black**
	Carbon (percentage of air-dry material)		
Cellulose	41·8	41·8	41·7
Starch	38·6	38·5	38·3
Pectin	34·4	32·8	32·4
Sodium alginate	27·9	24·2	21·5
Casein	46·9	41·7	33·5
Edestin	45·2	41·4	31·4
Oat Straw	39·8	41·7	39·5
Wheat Straw	41·6	41·5	40·7
Ryegrass I	39·6	40·9	38·3
Ryegrass II	40·3	40·7	38·1
Meadow fescue	36·7	38·1	37·7
Lignin I	62·7	64·0	63·3
Lignin II	62·1	65·2	64·6
Tannic acid	45·0	41·2	40·4
Humic acid	52·1	47·0	43·7
Ligno-protein	45·0	46·5	37·2
Compost	35·8	34·8	34·1
Chitin	44·4	37·0	33·5

* Results reported are actual, not corrected, values.

Table 3 shows the carbon contents of a range of organic materials, mostly derived from either plants or soils, determined by the Shaw, Tinsley, and Walkley and Black methods. There is good agreement between the Tinsley and Shaw methods on the carbon contents of cellulose and starch, and, allowing for the larger sampling error, agreement is also good with the whole plant materials and the compost. However, with casein, edestin, chitin, tannic acid, humic acid, pectin, and sodium alginate the Tinsley results are lower than the Shaw results: with lignin they are higher. The uncorrected Walkley and Black results were very similar to those of the Tinsley method, except for casein, edestin, ligno-protein, and chitin, where the results were much lower. The Walkley and Black technique gives good results with all the whole plant materials investigated, and is a simple and rapid method for the routine determination of carbon in such materials. No correction factor is required when the Walkley and Black method is used on whole plant material.

Titrimetric carbon methods measure the oxygen required for complete oxidation of a compound to carbon dioxide, water, and ammonia. In calculating carbon contents from dichromate consumption it is assumed that in the complete oxidation of a compound two oxygen atoms are required per carbon atom, i.e. that 1 ml. N dichromate is equivalent to 3 mg. of carbon. With compounds like cellulose this assumption is

valid, but with the lignins more than two oxygen atoms are required to oxidize a carbon atom and with the proteins less, because of the initial level of oxidation in these materials. Most of the materials listed in Table 3 are heterogeneous and their oxidation level cannot be calculated without complete elemental analysis. To see if the Tinsley method accurately measured the amount of oxygen required for complete oxidation of organic materials, a number of pure compounds of various oxidation levels were analysed, parallel tests being run by the Walkley and Black method. The results are shown in Table 4. Column 3 of this table gives the theoretical carbon content of the compounds analysed and column 6 the carbon content expected by both Tinsley and Walkley and Black methods if (*a*) the end products of the reaction are as postulated in column 4, (*b*) oxidation is quantitative, and (*c*) each equivalent of dichromate oxygen consumed is equivalent to 3 g. carbon, whether this be so or not. For the Tinsley method the agreement between expected carbon content and that found is within experimental error. This is also true of the Walkley and Black method except with aspartic acid and glycine, where oxidation is not complete, i.e. condition (*b*) above is not fulfilled. By analogy it is probable that the low results obtained with proteins (Table 3) by Walkley and Black's method are due to incomplete oxidation.

Table 4 indicates that discrepancies between the carbon contents of the materials listed in Table 3 as determined by the wet combustion and Tinsley methods are at least partially due to the levels of oxidation of the materials themselves. The close agreement between the results of the Tinsley, Walkley and Black, and Shaw methods on whole plant materials is probably due to compensation of errors in the titrimetric methods, lignin in the plant material raising the result and protein lowering it.

Soils are more complex; chlorides, ferrous iron, and active manganese oxides interfere with any method based on the titration of unused dichromate (Jackson, 1958), but none of these is likely to be present in significant amounts in any of the soils described in Table 1. The discrepancies between the results obtained on certain soils by the Tinsley and Shaw methods (Table 2) could be due to the level of oxidation of the soil organic matter differing from that of elemental carbon, i.e. the conversion factor 1 ml. N $K_2Cr_2O_7 \equiv 3$ mg. carbon used in calculating the Tinsley results did not hold. This was tested by determining both the dichromate consumed and the CO_2 evolved when three non-calcareous soils were analysed by Tinsley's method. The CO_2 evolved during a Tinsley oxidation (scaled up three times to give sufficient CO_2 for accurate gravimetric estimation) was absorbed in a train identical with that used in the Shaw method. The results (Table 5) showed that the discrepancies between the results obtained by the Shaw and Tinsley methods were partly due to the incomplete oxidation of soil organic matter to carbon dioxide in the Tinsley method and partly to the use of the factor 1 ml. N $K_2Cr_2O_7 \equiv 3$ mg. carbon in calculating the Tinsley results. In all three soils the organic matter was at a higher level of oxidation than that of elemental carbon. Table 2 shows that although the Tinsley method gives results which are, on average, slightly lower than

TABLE 4

Determination of Carbon in Organic Compounds by the Tinsley and the Walkley and Black Titration Methods

Compound	*Molecular formula*	*Theoretical carbon content (%)*	*Products of oxidation*	*No. of oxygen atoms required to oxidize one molecule*	*Carbon content (%) by titration methods*		
					*Expected**	*Found*	
						Tinsley	*Walkley and Black*
Glucose	$C_6H_{12}O_6$	40·0	$6CO_2 + 6H_2O$	12	40·0	40·2	40·3
Sucrose	$C_{12}H_{22}O_{11}$	42·1	$12CO_2 + 11H_2O$	24	42·1	42·0	42·2
Oxalic acid (dihydrate)	$C_2H_2O_6$	19·0	$2CO_2 + 3H_2O$	1	4·75	4·80	4·73
Citric acid (monohydrate)	$C_6H_{10}O_8$	34·3	$6CO_2 + 5H_2O$	9	25·7	25·5	25·5
Tartaric acid	$C_4H_6O_6$	32·0	$4CO_2 + 3H_2O$	5	20·0	20·8	20·4
Resorcinol	$C_6H_6O_2$	65·5	$6CO_2 + 3H_2O$	13	71·0	70·8	71·5
Catechol	$C_6H_6O_2$	65·5	$6CO_2 + 3H_2O$	13	71·0	70·8	71·4
Pyrogallol	$C_6H_6O_3$	57·2	$6CO_2 + 3H_2O$	12	57·2	56·9	57·2
Diphenylamine	$C_{12}H_{11}N$	85·3	$12CO_2 + 4H_2O + NH_3$	28	99·5	97·4	99·5
Glycine	$C_2H_5O_2N$	32·0	$2CO_2 + H_2O + NH_3$	3	24·0	24·8	0·73
Aspartic acid	$C_4H_7O_4N$	36·1	$4CO_2 + 2H_2O + NH_3$	6	27·1	27·1	3·7
Urea	CH_4ON_2	20·0	$CO_2 + 2NH_3$	0	0	1·7	0·07

* Results of titration methods are calculated on the arbitrary basis that two atoms of oxygen (supplied by dichromate) are required for oxidation of one atom of carbon. Thus if oxidation by dichromate is quantitative, and the end-products are as postulated in column 4, the expected carbon content (%) by titration methods

$$= \text{theoretical carbon content (\%)} \times \frac{n}{n_1 \times 2}$$

where n = number of oxygen atoms actually required to oxidize one molecule (column 5), and n_1 = number of carbon atoms per molecule.

TABLE 5

The Determination of Organic Carbon in Soils by the Tinsley Method: Recovery of Carbon by Titration of the Unused Dichromate and by Gravimetric Estimation of the CO_2 evolved

	*Recovery of carbon (%)**	
Soil	*Titrimetric*	*Gravimetric*
3	93·8	95·8
9	88·4	94·0
14	86·6	95·6

* Expressed as a percentage of the carbon content of the soils as found by wet combustion (Table 2).

those of wet combustion, the discrepancies do not show a consistent trend and no advantage is to be gained by multiplying the results by a correction factor as is done in the Walkley and Black method.

Acknowledgements

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REFERENCES

BREMNER, J. M. 1949. Analyst, **74,** 492.
—— and SHAW, K. 1958. J. Agric. Sci. **51,** 22.
COLLINS, S. H. 1906. J. Soc. chem. Ind., Lond. **25,** 518.
FORSYTH, W. G. C. 1947. J. Agric. Sci. **37,** 132.
JACKSON, M. L. 1958. Soil Chem. Analysis. Prentice Hall, New Jersey.
JENKINSON, D. S., and TINSLEY, J. 1959. Soil Sci. **10,** 245.
RICKSON, J. B. 1948. Analyst, **73,** 268.
SHAW, K. 1959. J. Soil Sci. **10,** 316.
TINSLEY, J. 1950. Trans. IV Int. Cong. Soil Sci. **1,** 161.
WALKLEY, A. 1935. J. Agric. Sci. **25,** 598.
—— and BLACK, I. A. 1934. Soil Sci. **37,** 29.

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DETERMINATION OF ORGANIC CARBON IN SOIL

II. EFFECT OF CARBONIZED MATERIALS

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Summary

A variable, and often substantial, amount of the carbon in carbonized materials, such as coal, charcoal, and graphite, is oxidized when these materials are treated with acid dichromate under conditions used in determining soil organic carbon. It is concluded that these methods cannot be used to detect carbonized materials in soil or to discriminate between carbon in carbonized materials and carbon in soil humus.

Introduction

CERTAIN cultural practices such as the firing of wood and scrub before cultivation, the burning of stubble after combine harvesting, the addition of soot, the application of crude fertilizers containing coal and clinkers all add carbonized materials to the soil. These materials are usually described as 'inert' or 'elemental' carbon and are believed to play little part in the carbon cycle of soil. Methods of analysing soil which will discriminate between the carbon in such materials and that in the plant residues and microbially synthesized organic materials which constitute soil humus are clearly of value, particularly if the turnover of humus carbon in soil is being investigated. It is commonly assumed, and often stated, that the rapid dichromate titration methods of determining organic carbon in soil afford such discrimination, but the sole evidence for this is that of Walkley (1947), who showed that only 2–11 per cent. of the carbon in gas coke, bituminous coal, wood charcoal, and native graphites was recovered by the Walkley and Black titration method of determining carbon in soil. Walkley suggested that Schollenberger's method might give even lower recoveries, and referred to work which led Allison (1935) to conclude that inert forms of carbon such as coal and clinkers may be estimated from the difference between total carbon as determined by dry combustion and organic carbon as estimated by his modified Schollenberger method. However, Allison's conclusion was based on indirect evidence, and it could not be confirmed by Shaw (1959), who found that Allison's version of the Schollenberger method was seriously affected by coal and charcoal. Shaw also found that coal interfered with his wet combustion method of determining organic carbon in soil, but that it was not oxidized as rapidly as soil organic matter under his conditions. He suggested that slow evolution of carbon dioxide on prolonged digestion of soil with the combustion mixture used in his technique indicates that the sample contains a considerable amount of coal or other carbonaceous material.

The object of the work described in this paper was, firstly, to test the conflicting statements on the oxidation of carbonized materials by acid

dichromate, and secondly, to see if the Tinsley method for the determination of organic carbon in soil was capable of discriminating between 'carbonized' and 'humus' carbon.

Experimental

Materials

Analyses of the carbonized materials used are given in Table 1. Carbon and hydrogen were determined by dry combustion (Weiler and Strauss, Oxford) and ash by ignition at 800° C. for 2 hours. Sugar charcoal, wood charcoal, coconut charcoal, synthetic graphite, and native graphite were obtained from British Drug Houses Ltd. The two

TABLE 1

Analysis of Carbonized Materials

Material	*Ash content* (%)*	*Carbon content* (%)†	*Hydrogen content* (%)†
Sugar charcoal . .	0·05	99·0	1·02
Wood charcoal . .	2·54	78·7	4·57
Coconut charcoal . .	13·6	97·0	2·59
Synthetic graphite . .	0·0	100·0	0·0
Native graphite . .	0·40	99·8	0·39
Anthracite coal . .	0·81	92·9	3·33
Bituminous coal . .	4·22	84·3	3·48
Soot	25·6	68·8	6·12

* Moisture-free basis. † Moisture- and ash-free basis.

samples of coal were obtained from Dr. A. H. Edwards; the sample of soot was from a domestic chimney. All the materials were ground to pass a 40-mesh sieve except the wood charcoal samples used in work on particle size (Table 4).

Methods

The techniques used to determine carbon were the methods for soil analysis described by Schollenberger (1927, 1931, 1945), Walkley and Black (1934), Tinsley (1950), and Shaw (1959). Details of the procedures followed using the Walkley and Black, Tinsley and Shaw methods are given in Part I of this series (Bremner and Jenkinson, 1960). Two versions of the Schollenberger method were used. They were essentially the modifications described by Allison (1935) and Jackson (1958). The former will be described as Schollenberger I, the latter as Schollenberger II.

Schollenberger I. A sample estimated to contain about 10 mg. of carbon was weighed into a Pyrex test tube (30 × 200 mm.) and treated with 0·3922 g. of finely ground $K_2Cr_2O_7$ (Analar) and 10 ml. of concentrated H_2SO_4. The mixture was heated with constant stirring so that it attained a temperature of 175° C. in about 90 seconds. The tube was then cooled and its contents poured into a 250 ml. flask containing 50 ml. of water, a further 100 ml. of water being used to rinse the

contents of the tube into the flask. Phosphoric acid (5 ml.: sp. gr. 1·75) was added and the residual dichromate determined by titrating with 0·2 N ferrous ammonium sulphate using barium diphenylamine sulphonate solution (5 ml.) as indicator

Schollenberger II. A sample estimated to contain about 10 mg. of organic carbon was treated in a Pyrex test tube (30 × 200 mm.) with 20 ml. of 0·4 N chromic acid solution, and the mixture was heated with

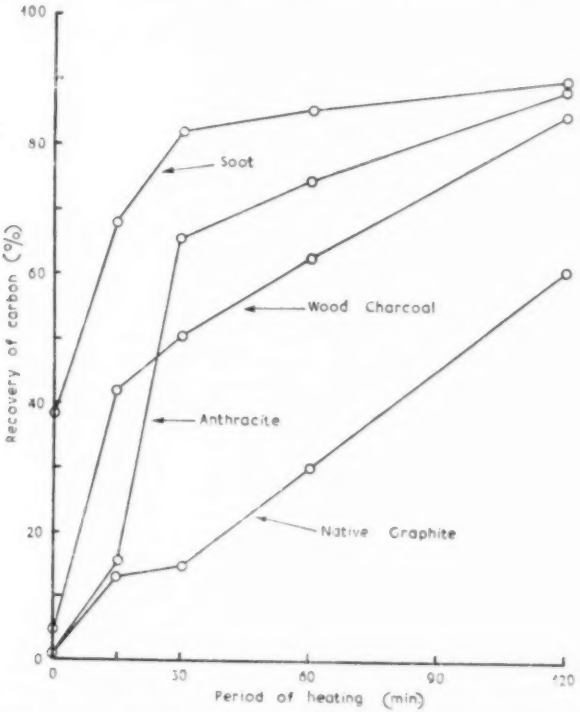

FIG. 1. Effect of varying the period of heating in analysis of various materials by the Tinsley method.

stirring so that it attained a temperature of 155° C. in 20–25 minutes. The temperature was held at 155–60° C. for 5 minutes, the tube was cooled, the contents were transferred with about 150 ml. of water to a 250 ml. conical flask, and H_3PO_4 (5 ml.: sp. gr. 1·75) was added. The residual dichromate was determined as in the previous method. The chromic acid solution used in this method was prepared by dissolving 19·61 g. of $K_2Cr_2O_7$ (Analar) in 50 ml. of water and diluting the solution to 1 litre with concentrated sulphuric acid.

The 0·2 N ferrous ammonium sulphate solution used in the two Schollenberger methods was prepared by dissolving 78·44 g. of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 300 ml. of water containing 20 ml. of

TABLE 2

Percentage of Carbon in Carbonized Materials Recovered by Different Methods of Determining Soil Carbon

Material	Method									
	Shaw		Tinsley		Schollenberger I		Schollenberger II		Walkley and Black	
	Average	Range	Average	Range	Average*	Range	Average*	Range	Average*	Range
Sugar charcoal	85	82–87	64	62–64	1 (1)	0–1	0 (0)	0	0 (0)	0
Wood charcoal	95	91–97	86	84–91	48 (55)	42–50	22 (24)	22–26	4 (5)	3–5
Coconut charcoal	95	94–95	96	95–97	64 (74)	63–65	33 (37)	32–35	36 (47)	35–39
Synthetic graphite	97	97–98	96	92–98	94 (108)	88–97	74 (82)	73–75	23 (30)	22–24
Native graphite	99	97–101	61	56–74	61 (70)	57–63	42 (47)	40–48	2 (3)	1–2
Anthracite coal	98	97–99	90	85–93	11 (13)	10–11	10 (11)	7–10	1 (1)	1–2
Bituminous coal	99	97–102	104	102–5	103 (118)	100–6	104 (115)	100–6	11 (14)	10–15
Soot	93	87–99	88	83–97	87 (100)	86–87	84 (93)	84–85	57 (74)	54–66

* Figures in parentheses are recoveries multiplied by appropriate correction factor (Schollenberger I, × 1·15; Schollenberger II, × 1·11; Walkley and Black, × 1·30).

TABLE 3

Effect of Varying the Period of Heating in Analysis of Carbonized Materials and Soils by the Shaw Method

Material	Period of heating (minutes)				
	3	7	10	15	30
	Percentage recovery of carbon				
Wood charcoal	93	97	96	98	97
Native graphite	99	100	99	99	98
Anthracite coal	95	100	98	100	100
Bituminous coal	97	97	99	100	101
Soil 3*	98	99	100	100	100
Soil 11*	97	98	99	100	100

* For a description of these soils, see Bremner and Jenkinson (1960).

TABLE 4

Effect of Particle Size of Sample on Analysis of Wood Charcoal by the Tinsley Method

Particle size	Recovery of carbon (%)	
	Average	Range
20–40 mesh	50	36–64
40–80 mesh*	87	73–94
Less than 80 mesh*	93	90–95

* Prepared from the 20–40 mesh material.

concentrated H_2SO_4 and diluting to 1 litre with water. The indicator solution was prepared by dissolving 0·3 g. of barium diphenylamine *p*-sulphonate and 58·7 g. of $BaCl_2.2H_2O$ (Analar) in 1 litre of warm water and filtering the cooled solution.

When the Schollenberger and Walkley and Black titration methods are used to estimate carbon in soil, the results (calculated on the basis that 3 mg. of carbon consumes 1 ml. of N $K_2Cr_2O_7$) are multiplied by an empirical factor to correct for incomplete recovery of soil carbon by

these techniques. The factors used here were as follows: Schollenberger I, 1·15 (Allison, 1935); Schollenberger II, 1·11 (Jackson, 1958); Walkley and Black, 1·30 (Walkley, 1935).

Results

Table 2 shows the percentages of the carbon in the carbonized materials recovered by the Shaw, Tinsley, Schollenberger, and Walkley and Black methods of determining carbon in soil.

The effects of varying the period of heating in analysis of carbonized materials by the Shaw and Tinsley methods are shown in Table 3 and Fig. 1, respectively. For comparison, the results of analyses of two soils by the Shaw method are also reported in Table 3. Table 4 shows the effect of the particle size of the sample on analysis of wood charcoal by the Tinsley method.

Discussion

The results in Table 2 show that all of the methods tested recover a significant amount of the carbon in carbonized materials and that they cannot discriminate between the carbon in such materials and the carbon in soil humus. With the exception of bituminous coal, the recovery of carbon by the dichromate titration methods was lowest with the Walkley and Black method and highest with Tinsley's method. This is probably because the period of heating in the methods tested decreases in the order: Tinsley > Schollenberger > Walkley and Black. The only apparent explanation for the recovery of carbon in bituminous coal being as high by the two Schollenberger techniques as by the Tinsley method is that a violent reaction occurs when bituminous coal is oxidized by either of the Schollenberger methods. This may lead to thermal decompositon of dichromate and thus cause the results to exceed theoretical.

Table 4 shows that the oxidation of carbon in carbonized materials by acid dichromate takes place at the surface of the particles, the oxidation of wood charcoal by the Tinsley method increasing with decrease particle size of the material analysed. A portion of all the carbonized materials listed in Table 1 floated on the surface of the oxidation mixture, and this almost certainly explains the spread of the results given in Table 2. Flotation was particularly noticeable with the charcoals.

The slow liberation of carbon dioxide detected by Shaw (1959) in analysing coal by his wet combustion method was not observed with the carbonized materials used in our work (Table 3) and is not, therefore, a reliable indication of the presence of carbonized materials.

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REFERENCES

Allison, F. E. 1935. Soil Sci. **40**, 311.
Bremner, J. M., and Jenkinson, D. S. 1960. J. Soil Sci. **11**, 394.
Jackson, M. L. 1958. Soil Chemical Analysis. Englewood Cliffs: Prentice-Hall.

RILEY, H. L. 1938. Trans. Faraday Soc. **34,** 1011.
SCHOLLENBERGER, C. J. 1927. Soil Sci. **24,** 65.
—— 1931. Ibid. **31,** 483.
—— 1945. Ibid. **59,** 53.
SHAW, K. 1959. J. Soil Sci. **10,** 316.
TINSLEY, J. 1950. Trans. 4th Int. Cong. Soil Sci. **1,** 161.
WALKLEY, A. 1935. J. Agric. Sci. **25,** 598.
—— 1947. Soil Sci. **63,** 257.
—— and BLACK, I. A. 1934. Ibid. **37,** 29.

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TOTAL ELEMENTS IN TOPSOILS FROM IGNEOUS ROCKS: AN EXTENSION OF GEOCHEMISTRY[1]

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Summary

The amounts of eighteen elements Al, Fe, Mg, Ca, Na, K, Ti, Zr, Cr, Ni, Co, Mn, Mo, Ga, Cu, V, Sr, Ba, in topsoils from igneous rocks of the South-West Pacific region have been related to the nature of the parent rock, the degree of soil weathering, and the organic-matter content.

When the mineral topsoils are only weakly weathered the total-element contents are directly related to geochemistry. In strongly weathered topsoils the geochemistry of primary minerals has largely been replaced by the chemistry of secondary minerals. In combining analyses of topsoils having varying degrees of weathering within the parent-rock groupings ultrabasic, basaltic, andesitic, and rhyolitic, the amounts of the elements are greatly modified by soil-forming processes, but the distribution trends inherited from magmatic fractionations remain for Fe, Mg, Na, K, Ti, Cr, Ni, Co, Mn, Mo, Cu, V, Sr, Ba.

The leaching or concentration of elements during soil weathering was traced from the build-up of clay within parent-rock groupings. Under the high rainfalls of the region soil weathering was accompanied by loss of Mg, Ca, Na, K, Sr, Ba, resulting in a concentration of Fe, Ti, Mo, Ga, V, and little, or irregular, change in Al, Zr, Cr, Ni, Co, Mn, Cu.

The leaching of elements in soils derived from acidic rocks can be modified by litter from vegetation such as kauri (*Agathis australis*). In strongly podzolized, strongly weathered topsoils with a kauri cover the elements normally concentrated under climatic weathering have been removed by vegetative leaching, and silicon is the residual element.

Organic topsoils had lower element contents (on oven-dry weight) than the mineral-organic soils.

Introduction

THE South-West Pacific is a region of volcanic rocks from which many soils have inherited their chemical properties. Igneous rocks cover a quarter of the land surface, but veneers of volcanic ash ... over a wider area. The surface area of 35,000 square miles of igneous rocks is made up as follows:

Ultrabasic	8%
Basaltic	26%
Andesitic	34%
Rhyolitic	29%
Granitic	3%

Topsoils analysed were from climatic zones ranging from the subantarctic to the tropics and included the islands Campbell, Auckland, Chatham, New Zealand, Norfolk, Fiji, Samoa, Cook, New Caledonia, and Solomon. The selection of sites has been guided by the genetic soil map of New Zealand (Taylor, 1948).

[1] Soil Bureau Publication No. 208.

Fractionation of minerals in the magmas has set the element levels at which soil development commenced. The combination of age of eruption and climatic processes has resulted in topsoils at various stages of weathering. The weathering processes, in this region of high rainfall, have resulted in losses of certain elements and the consequent concentration of others. In grouping topsoils for their total element content emphasis is placed on the transition from the geochemistry of primary minerals in rocks to the chemistry of secondary minerals in soils.

Generalizations on the geochemical distribution of elements in igneous rocks have been made by Goldschmidt (1954), and Sandell and Goldich (1943). In tables of mean major element composition of volcanic rocks Daly (1933) has shown that decreasing silica (rhyolite to basalt) is accompanied by increasing Fe, Mg, Ca, Ti, Mn contents and decreasing Na, K contents. In a detailed study of the Skaergaard intrusion, Wager and Mitchell (1951) have shown the trend of minor elements in the fractionation of a basic magma to be:

early, low silica,	fractions	concentrate	Cr, Ni (Co, Mo)
middle	,,	,,	V, Cu, Mn (Co, Sr)
late, high silica	,,	,,	Zr, Ba (Ga, Mo).

The changes that took place with increasing degrees of soil development will be discussed in groupings made according to the nature of the parent rock. As only total element levels are being measured, these groupings are not intended to express agricultural aspects of soils.

Methods

The topsoils analysed, A horizons 6 in. or less deep, were mainly collected during the New Zealand Soil Bureau surveys. After oven-drying, to provide a standard basis for expressing the results, the samples were ignited at 500° C. for one hour. They were ground and diluted 1 : 1 with carbon and analysed spectrographically by a semi-quantitative method using the cathode layer emission (Mitchell, 1948). The accuracy of the analyses was only ±30 per cent. but interest lies in mean values from several sites and with major variations in element content.

The spectrographic lines (Å.) used for the analyses were:

Al	3,944·0		Ti	3,989·8		Mo	3,170·3	
Fe	3,306·0/3,440·6		Zr	3,438·2		Ga	2,943·6	
Mg	2,779·8		Cr	4,254·3		Cu	3,247·5	
Ca	4,226·7		Ni	3,414·8		V	4,379·2	
Na	3,302·3		Co	3,453·5		Sr	4,077·7	
K	4,044·1		Mn	4,030·8		Ba	4,554·0	

Other elements investigated by the same spectrographic method were Ag, Pb, Sn; as they were at the limit of their detectability (1, 10, 10 p.p.m.) the results have not been reported in the tables. For a few topsoils the K 4,044·1 line was insufficiently sensitive, and the potassium measurements were made by a flame photometer after hydrofluoric-sulphuric acid digestion of the soils. The Mo 3,170·3 line could not be used in the presence of very high levels of iron due to interference by Fe

3,170·3. The molybdenum contents of the topsoils from ultrabasic and some of the basaltic rocks were determined by a molybdenum thiocyanate colorimetric method. The silicon measurements were made on composite samples by a fusion followed by two hydrofluoric acid treatments.

Results

Topsoils in which mineral matter is the major constituent are grouped under the parent-rock headings reported by soil surveyors; in addition, a unit has been made of the topsoils in which organic matter is dominant.

The sites may have been subject to the influences of soil creep but alluvial depositions, with the possibility of mineral resorting, have been excluded.

The mean total analyses for the topsoils from igneous rocks are presented in Table 1. Topsoils low in organic matter had an average loss on ignition of 28 per cent. after drying at 110° C., compared with 70 per cent. for the topsoils high in organic matter. On an oven-dry weight basis topsoils of high organic matter content had lower amounts of Al, Fe, Mg, Ca, Na, K, Zr, Mo, Ga than any group having low organic matter content. The element contents of the topsoils low in organic matter strongly reflected the influence of their parent rock. The ignited topsoils had silica contents (rhyolite 62, andesite 49, basalt 36, and ultrabasic 26 per cent.) that were approximately 10 per cent. lower than the average values for igneous rocks (Daly, 1933).

In the topsoils low in organic matter a decrease in the silica levels of the igneous rocks, rhyolite to ultrabasic, was accompanied by an increasing content of Fe, Mg, Cr, Ni, Co. Ti, Mn levels had a peak at the basalt stage, V at the basalt-andesite stages, and Cu, Sr at the andesite stage, while Na, K, Ba increased in the topsoils with increasing silica in the rocks.

The trends in the element distribution inherited from the parent rocks remain in the topsoil mean analyses for the elements Fe, Mg, Na, K, Ti, Cr, Ni, Co, Mn, Mo, Cu, V, Sr, Ba. The actual values, however, are modified by the soil-forming process. Under the high rainfall conditions of the region (sites averaged 65 in. per annum with only two below 30 in.) the topsoils low in organic matter had less Mg, Ca, Na, K than the geochemical values (Daly, 1933). The exception is in the rhyolite group which, through the inclusion of dacite members, had slightly high Mg, Ca values.

The usefulness of the mean values in Table 1 is limited since it does not take into account the loss of certain elements from the topsoils by leaching processes during the weathering of minerals and the consequent concentration of other elements. The total element content of young weakly weathered topsoils depended upon the primary minerals present, while in the strongly weathered topsoils it was related to the secondary clay minerals. To isolate the effects of leaching and concentration that have taken place within the parent-rock groupings, it was necessary to adopt some index of weathering. The texture groupings of the topsoils can be used to represent the transition during weathering from primary to secondary minerals.

TABLE 1

Total Analyses of Topsoils from Igneous Rocks

Organic matter content	*Parent rock*	*No. sites*	Al	Fe	Mg	Ca	Na	K	Ti	Zr	Cr	Ni	Co	Mn	Mo	Ga	Cu	V	Sr	Ba
			%			%			p.p.m.											
	Ultrabasic	5	6·0	17	4·8	1·2	0·62	0·28	1,500	200	9,400	3,100	320	3,300	1·3	9·0	40	120	40	100
	Basalt	38	11	11	1·5	1·3	0·67	0·34	16,000	570	540	130	39	4,000	3·4	39	61	210	130	130
LOW	Andesite	33	10	8·3	1·1	1·5	0·99	0·58	5,700	530	81	14	22	1,300	2·1	30	92	200	300	420
	Rhyolite	39	10	3·0	0·73	1·6	1·6	1·2	3,100	590	11	2·6	3·6	2,500	3·0	22	15	51	280	970
	Granite	3	6·0	2·6	0·50	1·1	1·7	2·1	2,500	330	9	1·3	0·30	130	1·0	15	12	27	500	1,000
HIGH	Various	16	1·5	1·1	0·35	0·42	0·36	0·32	2,100	150	70	4·3	1·5	210	1·0	6·4	25	28	180	400

TABLE 2

Total Analyses of Topsoils Low in Organic Matter from Ultrabasic Rocks

Topsoil texture	*No. Sites*	Al	Fe	Mg	Ca	Na	K	Ti	Zr	Cr	Ni	Co	Mn	Mo	Ga	Cu	V	Sr	Ba
		%			%			p.p.m.											
Silt and stony clay loams .	3	6·7	12	7·7	2·0	1·0	0·40	1,500	180	9,000	2,300	270	3,500	00·6	8·3	34	77	70	170
Clay . .	2	4·5	24	0·50	0·10	0·05	0·09	1,400	230	15,000	5,200	400	2,800	2·3	10	50	180	10	<20

TABLE 3

Total Analyses of Topsoils Low in Organic Matter from Basalts

Topsoil texture	*No. sites*	Al	Fe	Mg	Ca	Na	K	Ti	Zr	Cr	Ni	Co	Mn	Mo	Ga	Cu	V	Sr	Ba
		%						p.p.m.											
Sand	0	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sandy loam	6	5·6	10	5·3	4·4	1·7	0·80	17,000	360	530	370	65	1,900	1·5	16	58	160	350	270
Silt loam	7	13	9·0	1·8	1·1	0·80	0·50	10,000	500	160	44	24	1,800	3·1	36	73	180	220	240
Clay loam	13	11	9·2	0·87	0·70	0·46	0·20	11,000	850	300	68	19	900	3·4	47	59	150	85	100
Clay	12	14	16	0·78	0·43	0·30	0·22	24,000	410	1,100	110	58	9,200	4·2	48	60	330	7·5	35

TABLE 4

Total Analyses of Topsoils Low in Organic Matter from Andesites

Topsoil texture	*No. sites*	Al	Fe	Mg	Ca	Na	K	Ti	Zr	Cr	Ni	Co	Mn	Mo	Ga	Cu	V	Sr	Ba
		%						p.p.m.											
Sand	5	7·7	4·6	2·1	2·8	2·0	1·2	3,800	360	53	10	21	1,200	1·0	26	100	200	560	780
Sandy loam	3	12	5·3	2·3	2·9	1·9	1·1	3,700	330	47	6·0	25	1,700	2·0	33	100	220	570	770
Silt loam	10	12	7·7	1·1	1·7	1·2	0·60	5,700	460	31	3·6	17	1,600	2·2	30	89	190	380	590
Clay loam	8	10	9·8	0·70	0·70	0·50	0·50	5,400	680	190	35	29	1,400	3·1	28	98	160	86	200
Clay	7	9·0	11	0·50	0·30	0·20	0·20	8,300	670	71	9·0	23	670	2·1	33	80	260	18	19

Weathering of the fine-grained volcanic rocks proceeded rapidly with a build-up of clay which could be expressed in terms of the topsoil texture. Rocks with large particles of resistant primary minerals (such as quartz) that weather to coarse-textured rather than to fine-textured soils, are not common in the volcanic region. Texture groupings can thus be used as a weathering index provided it is recognized that secondary minerals can give rise to a coarser 'secondary' soil texture. In advanced stages of weathering the clay soils from basalt assume a loamy texture and, in the extreme, become gravelly due to nodulation of secondary minerals such as gibbsite. In this study such secondary gravelly soils are grouped with the clay soils. It was necessary to exclude sites of alluvial deposition since re-sorting of mineral particles can give coarse soil textures composed of resistant primary minerals such as quartz, zircon, ilmenite, and magnetite.

The topsoil texture groupings adopted for the weathering index were: sands, sandy loams, silt loams (including loams), clay loams, and clays. It is not implied that the topsoils had necessarily proceeded through all the prior coarser textures in turn. The weakly weathered sands and sandy loams were found on the volcanic ashes rather than the flows; the strongly weathered soils occurred on all forms of erupted rocks. The numerical distribution of sites within the parent-rock groupings is given in the Tables 2 to 5, and show that the topsoils from the basic rocks were advanced in weathering, while weakly weathered topsoils were more common on andesitic and rhyolitic ashes.

The topsoil total analysis will be considered under the groupings of Table 1, and under individual elements for the soils low in organic matter.

Groupings

Ultrabasic

The ultrabasic igneous rocks, having olivine minerals with high amounts of iron and magnesium, give rise to topsoils having 10 to 100 times the normal values of the minor elements Cr, Ni, Co; Robinson, Edgington and Byers (1935), Birrell and Wright (1945), and Lounamaa (1956). In Table 2 the topsoils from ultrabasic rocks have been grouped in two stages of weathering, silt loam plus stony clay loams (pH 7) of New Zealand, and clays plus nodulated clays (pH 5·5) of New Caledonia and Solomon. Irrespective of weathering zone these topsoils have high contents of Fe, Cr, Ni, Co, and low contents of Al, Na, Zr, Ga. Under tropical conditions, where the degree of weathering and leaching is high, Mg, Ca, Na, K, Sr, Ba levels were lower than under the temperate conditions of New Zealand. The topsoils in the tropics had higher levels of Fe, Cr, Ni, Co, Mo, V, indicating the resistance of these elements to the leaching processes that removed the bases.

Basaltic

The olivine basalts occur in the region principally as flows but scorias and ashes are also present. The element contents of the weakly weathered topsoils are related to the presence of calcic plagioclase, augite, and olivine minerals. Weathering and soil development, as expressed by the build-up

of clay in Table 3, were accompanied by losses of the elements Mg, Ca, Na, K, Sr, Ba. The pH range of the samples was from 7·0 to 5·0, with the majority of the topsoils below 6. The highest amounts of Al, Fe, Ti, Cr, Mn, Ga, V occurred in the clay soils that had lost their bases by leaching processes. The Samoan basalts tended towards an ultrabasic composition and their topsoils had higher Cr, Ni, Co contents than the other sites.

A good example of soil weathering without considerable loss of bases occurs outside the region in the Darling Downs of Australia. There the black clay soil (montmorillonite type) pH 6, formed on basalt colluvium in contrast to the red clay soils (hydrated kaolin and/or gibbsite) of the South-West Pacific, had levels of Mg, Ca, Na, K, Ba that were similar to the silt loam stage, rather than the clay stage, of Table 3.

Andesitic

The element contents of weakly weathered topsoils from andesitic ashes and flows are related to the presence of minerals such as andesine, augite, hypersthene, and hornblende. The mean element content of these topsoils (Table 1) were intermediate between those from basalt and from rhyolite for the elements Fe, Mg, Ca, Na, K, Ti, Cr, Ni, Co, V, Ba. During weathering on andesitic materials (Table 4) the elements Mg, Ca, Na, K, Sr, Ba were lost by leaching while the more resistant elements Fe, Ti, Zr tended to concentrate. The pH levels of the topsoils ranged from 6·5 to 4·5.

Rhyolitic

The rhyolite group was a composite one which included ashes and rocks tending towards dacite. The primary crystalline minerals were quartz and feldspars with minor amounts of ferro-magnesian minerals; glassy minerals were present in the pumices. The low contents of Fe, Mg, Ti, Cr, Ni, Co, Cu, V in the topsoils resulted from the separation or capture of these elements at an earlier stage in the magmatic fractionation. Elements remaining, such as Na, K, Zr, Ba, were consequently concentrated in the rhyolitic fraction.

Weathering, as indicated in Table 5, was accompanied by losses of the elements Ca, Na, K, Sr, Ba, whilst the clay soils had the highest levels of Fe, Ti, Co. The pH range of the topsoils was from 6·5 to 5·0. Recent eruptions have ejected rocks more rhyolitic than the older, more weathered members and this is reflected in low levels of Mg, Cr, Co in the weakly weathered, sandy topsoils.

Topsoils of podzols, A_0 horizons including mors, occurring on the acidic rocks have been included in the group having high amounts of organic matter. Where the podzol has been cleared of vegetation, and depleted of its organic matter, a topsoil of high silica content has formed (loss on ignition, after oven-drying, 5 per cent.). The topsoil (0 to 6 in.) of such a podzol, developed under a previous forest of kauri (*Agathis australis*), had the element levels as follows:

Al 0·5, Fe 0·1, Mg 0·02, Ca 0·06, Na 0·5, K 0·3,%; Ti 600, Zr 200, Cr 2, Ni < 1, Mn 30, Co < 1, Mo < 1, Ga 5, Cu 2, V < 5, Sr < 10, Ba < 10, p.p.m.

TABLE 5
Total Analyses of Topsoils Low in Organic Matter from Rhyolites Plus Dacites

Topsoil texture	*No. sites*	Al	Fe	Mg	Ca	Na	K	Ti	Zr	Cr	Ni	Co	Mn	Mo	Ga	Cu	V	Sr	Ba
		%						p.p.m.											
Sand	11	6·5	1·8	0·60	2·2	2·1	1·4	2,700	470	5·8	2·3	1·5	1,100	1·5	15	5·7	34	390	1,300
Sandy loam	12	11	2·7	0·80	2·0	2·0	1·4	3,000	550	11	1·0	3·0	3,800	3·3	22	14	51	330	940
Silt loam	8	13	2·7	0·75	1·6	1·5	1·4	3,100	700	7·7	3·0	4·0	4,500	4·7	23	18	46	290	1,400
Clay loam	2	11	5·6	0·60	0·80	0·60	1·2	3,000	300	28	1·5	6·0	400	2·0	27	35	75	15	75
Clay	5	7·0	5·8	0·70	0·66	0·36	0·18	4,400	600	17	4·7	8·0	640	3·0	31	23	88	51	56

TABLE 6
Total Analyses of Topsoils High in Organic Matter

Topsoils high in organic matter	*No. sites*	*% loss on ignition*	Al	Fe	Mg	Ca	Na	K	Ti	Zr	Cr	Ni	Co	Mn	Mo	Ga	Cu	V	Sr	Ba
			%						p.p.m.											
Over basalt	6	86	0·03	1·7	0·28	0·23	0·14	0·16	3,200	22	170	9·4	3·2	95	1·4	5·6	31	28	150	58
,, andesite	4	50	4·2	1·5	0·82	0·80	0·51	0·42	2,600	100	22	2·6	4·4	610	1·3	13	43	62	260	300
,, rhyolite	6	66	0·90	0·21	0·12	0·36	0·42	1·0	630	260	0·73	0·32	0·25	49	0·45	2·6	6·1	4·8	150	840
Organic	8	93	0·30	0·12	0·25	0·31	0·15	0·07	440	19	2·5	3·4	0·75	93	1·0	0·47	24	3·0	180	60
Mineral-organic	8	46	3·1	2·1	0·46	0·53	0·53	0·65	3,700	290	160	5·2	4·1	320	1·1	12	25	53	180	770

The parent rock was a quartz-rich dacite having element levels similar to the weakly weathered topsoils of Table 5. The combination of strong weathering and strong podzolization resulted in a concentration of silica in the topsoil and a decrease in all the elements measured. The texture of the podzol topsoil, a sandy loam, should not be confused with the sandy loam stage of the weathering index. Podzols reach a climax in New Zealand where the climate has been warm enough for kauri to thrive on the strongly weathered, strongly leached, soils while the temperatures are not sufficient to cause rapid mineralization of the litter. On the more basic volcanic rocks the rate of weathering is such that vegetation plays a minor role in the leaching process and hydrous oxides of iron, rather than silica, tend to accumulate in the topsoil (Taylor, Cunningham, and Davies, 1956).

Granitic

Three topsoils from granites in New Zealand have been given in Table 1. They were sandy loams, of pH 5, on two granites and a granodiorite. Their minor element contents were generally lower than those from rhyolite. Comparing the means at the same sandy loam topsoil texture (Tables 1 and 5) the topsoils on granite had lower Mg, Ca but higher K than on rhyolite. Manganese was outstandingly low on the granite topsoils.

It is not to be expected that granite will be as definite a unit of chemical composition as rhyolitic pumice where a true magmatic fractionation has taken place. For example, Lounamaa (1956) quotes topsoils over silicic rocks, that include granites, as having high contents of elements such as Cr, Co, Ni, Cu.

Organic

Soil cultivation, with its associated change in vegetation, has transformed the topsoils of about a third of the area from being high in organic matter to topsoils lower in organic matter. The degree to which the topsoils are organic can be conveniently expressed in terms of the loss on ignition after drying. Organic topsoils have been taken as those having losses on ignition greater than 90 per cent., as plant remains seldom have ash contents greater than 10 per cent. The remaining mineral-organic topsoils had losses on ignition, after drying, within the range 90 to 40 per cent., and averaged 46 per cent.

Table 1 lists the mean element contents, on an oven-dry weight basis, of sixteen topsoils high in organic matter. In Table 6 these have been subdivided in two ways, firstly according to the underlying volcanic rock, and secondly according to their organic matter content from loss on ignition. The soils high in organic matter over rhyolite include those over granite.

Topsoils low in organic matter (Table 1) have shown that the parent-rock sequence basalt-andesite-rhyolite was accompanied by a decrease in Fe, Mg, Ti, Cr, Ni, Co, Ga, and an increase in Na, K, Ba. The only elements that retained these trends in topsoils of high organic matter content (Table 6), Fe, K, Ti, Cr, Ni, Ba, were very strongly differentiated

in soils low in organic matter. The amounts of the elements were lowered by the build-up of organic matter. The low value of loss on ignition for those over andesite (Table 6) indicated a high mineral content, resulting in high levels of the major elements Al, Mg, Ca.

The organic topsoils with an average loss on ignition of 93 per cent. had lower element contents for those measured, apart from Mo, Sr, than the mineral-organic topsoils.

Individual Elements

Aluminium

Low levels of aluminium were found in the topsoils derived from ultrabasic rocks (Table 1) where iron-magnesium silicates take the place of aluminium silicates in the less basic rocks. Within the parent-rock groupings (Tables 3, 4, and 5) the mean aluminium contents gave a peak at the silt loam stages and indicated a slight relative concentration of the element at the early stages of soil weathering. This may be attributed to an allophanic association of silica and alumina formed from the volcanic ashes (Taylor, 1933). This association reaches a maximum in the loamy topsoils (pH 6) formed from andesitic ash. In the strongly weathered topsoils from rhyolite and andesite (pH 5·5 to 5) hydrated kaolin-type minerals are dominant (Fieldes, 1955) and the aluminium levels were slightly lower than at the higher pH levels of the less weathered soils. In the strongly weathered topsoils from basalt the high aluminium content of the clay soils is related to the presence of gibbsite in some of these soils (Fieldes and Swindale, 1954).

Iron

The basic igneous rocks commenced soil development with more iron than the acidic rocks; this is reflected in a fivefold difference between the iron contents of the weakly weathered soils from rhyolite and from basalt (Tables 3 and 5). Weathering of the primary minerals, as indicated by the texture groupings in Tables 2 to 5, proceeded with a build-up of iron in the topsoils. A concentration ratio for iron, expressed by the ratio of iron in the strongly weathered clay topsoils to that in the weakly weathered, sandy topsoils, was 2 on ultrabasic, 1·5 on basalt, 2·5 on andesite, and 3 on rhyolite.

Iron remained in the topsoils at pH levels (5 to 5·5) at which aluminium had been lost. Hough, Gile, and Foster (1941) considered that, in Hawaiian soils from basalt, aluminium was more soluble than iron at the more advanced stages of soil weathering. They found that at the young stages of soil development (pH above 6) the aluminium levels were greater than those of iron, while at low pH levels (5·2) the iron levels were greater than aluminium. In the topsoils from basalt (Table 3) the iron levels exceeded those of aluminium in the strongly weathered clay soils (pH 5·5).

Magnesium

The presence of olivine in the ultrabasic rocks gave topsoils in New Zealand with high magnesium contents (Table 2). These soils were a

silt loam and stony clay loams but the stones were excluded from the analyses. The difference in the magnesium content of these topsoils from ultrabasic rocks and weakly weathered topsoils from rhyolite (Table 5) was tenfold. Within the parent-rock groupings the degree to which magnesium was leached out, expressed as a leaching ratio of the element content in the weakly weathered topsoils to that in the strongly weathered topsoils, was 15 on ultrabasic, 7 on basalt, 4 on andesite, and 0 on rhyolite.

Calcium

The high calcium contents of the weakly weathered topsoils from basalt were related to the presence of minerals such as calcic plagioclase and augite, in contrast to the magnesium-rich olivine of the ultrabasic rocks, and the feldspars rich in sodium and potassium of the rhyolite. There were considerable losses of calcium during soil weathering; the leaching ratios were 20 on ultrabasic, 10 on basalt, 9 on andesite, and 3 on rhyolite.

Sodium

The highest mean sodium value occurred in the weakly weathered topsoils from rhyolite, but the differences between the weakly weathered topsoils from the three volcanic parent rocks were not great. Under the humid conditions soil weathering was accompanied by decreasing sodium contents with leaching ratios of 20 on ultrabasic, 6 on basalt, 10 on andesite, and 6 on rhyolite.

Potassium

The rhyolitic rocks with their potassium feldspar minerals had weakly weathered topsoils with up to twice the potassium content of weakly weathered topsoils from the more basic rocks. These differences inherited from the parent rock, as with sodium, were not as great as the changes that could take place during soil weathering. The leaching ratios for potassium were 0 on ultrabasic, 4 on basalt, 6 on andesite, and 8 on rhyolite. Although the leaching ratio was highest for topsoils on rhyolite their potassium content remained very constant during the early stages of soil weathering.

Titanium

The early, low silica, fractions of the Skaergaard intrusion contained less titanium than the magma (Wager and Deer, 1939) and the main deposition of the element awaited the separation of the iron ores. Small amounts entered the pyroxenes. In the topsoils from igneous rocks the mean titanium value reached a maximum in the soils from basalt (Table 1). Within the parent-rock groupings of Tables 3, 4, and 5 the strongly weathered clay soils had higher titanium contents than the weakly weathered topsoils and the element was considered to concentrate on soil weathering. This concentration of titanium was less marked and less consistent than the leaching of bases. Hough, Gile, and Foster

(1941) in a study of profiles on basalt concluded that titanium was more resistant to the leaching processes than aluminium or iron.

Zirconium

As with titanium the amount of zirconium entering the early, low silica, Skaergaard rocks was less than that in the magma (Wager and Mitchell, 1951). The mineral topsoils from the ultrabasic rocks (Table 1) had the lowest zirconium contents. There was a tendency for the levels of the element to increase with increasing degree of soil weathering, within the parent-rock groupings, up to the silt loam or clay loam stages. Zirconium had not concentrated, as did titanium, at the clay stage.

Chromium

Chromium showed a very marked differentiation between parent-rock groupings, varying from 9,400 p.p.m. in topsoils from ultrabasic rocks to 9 p.p.m. from granite. Chromium is associated with iron and magnesium as a chrome-spinel and is concentrated along with olivine in the early rock fractions. Chromium can also enter the pyroxenes (Wager and Mitchell, 1951). In the topsoils the highest levels of chromium were in the strongly weathered clays from ultrabasic and basaltic rocks.

Nickel

Nickel readily enters the magnesium-rich olivine minerals of the ultrabasic rocks (Sandell and Goldich, 1943). The low nickel content of later fractions of magmatic fractionation are due to lack of nickel in the residual magma rather than any difficulty of entry into late minerals (Wager and Mitchell, 1951).

Nickel, like chromium, showed a marked differentiation in the topsoils from igneous rocks (Table 1). No clear pattern of leaching or concentration emerged from the results of weathering within the parent-rock groupings.

Cobalt

The element cobalt is considered to be geochemically related to ferrous iron (Goldschmidt, 1954) and, like chromium and nickel, it was strongly differentiated in the mineral topsoils from igneous rocks. It readily entered olivines (Wager and Mitchell, 1951) reducing the cobalt content of the residual magma. Sandell and Goldich (1943) found that the distribution of cobalt in igneous rocks of varying silica content was more narrow than for nickel. In the topsoils from ultrabasic rocks cobalt does not reach the same high levels as chromium or nickel.

From the weathering stages within parent-rock groups the concentration or loss of cobalt on soil weathering was uncertain. Fujimoto and Sherman (1950) in a study of profiles on basalt found the highest cobalt levels in the A horizons. Their average cobalt content of topsoils from basalt, 36 p.p.m., agreed very closely with Table 1.

Molybdenum

Sandell and Goldich (1943) found that molybdenum in American igneous rocks increased with increasing silica content. However, Wager

and Mitchell (1951) found high levels of molybdenum in the olivine minerals at an early, low silica, stage of magmatic fractionation as well as in the granophyres of the later stages. The high molybdenum contents of the topsoils from igneous rocks (Table 1) was partly due to the concentration of the element that took place during soil weathering. The high molybdenum levels were found in the moderately weathered soils from rhyolite and in the strongly weathered soils from basalt.

Manganese

Manganese occurred mainly in the pyroxenes and olivines of the Skaergaard intrusion (Wager and Mitchell, 1951) and reached its lowest level of 150 p.p.m. in the acid granophyre. In the topsoils formed from igneous rocks (Table 1) high levels were found in soils from basalt and low levels in those from granite. There was a marked difference between the manganese content of the topsoils from rhyolite (mainly pumices) and from granites.

The weathering sequences on individual parent-rock groupings did not provide a generalized trend in the manganese levels. The strongly weathered clay topsoils from basalt attained very high levels of manganese similar to mature soils on basalt flow in Hawaii (Hough, Gile, and Foster, 1941). On the topsoils from andesite and rhyolite (Tables 4 and 5) manganese appeared to be lost during the weathering processes.

Gallium

Gallium is considered to be geochemically related to aluminium (Goldschmidt, 1954). Low levels of the element occur in olivine minerals of the early fractions of igneous rocks, but it can enter plagioclase and magnetite (Wager and Mitchell, 1951). In the mineral topsoils (Table 1) the lowest gallium contents were in those derived from ultrabasic rocks. The gallium levels tended to increase with increasing weathering within the parent-rock groupings. The highest gallium levels were found in the strongly weathered, gibbsitic clay soils from basalt.

Copper

The copper content of the topsoils reached a maximum in those derived from andesite (Table 1). Wager and Mitchell (1951) found that copper did not readily enter the early fractions of a basic magma and the main deposition occurred at the middle stages. No clear pattern of copper movement was found from soil weathering within the parent-rock groupings. In New Zealand the strongly weathered topsoils from basalt and andesite had half the copper content of the weakly weathered topsoils.

Vanadium

Wager and Mitchell (1951) found that vanadium occurred in pyroxenes and iron ores but not in olivines. The main precipitation of the element took place in magnetite at the middle stages of magmatic fractionation and resulted in a depletion of the element content of the residual magma.

The mean vanadium contents of the topsoils from igneous rocks (Table 1) reached high values in those formed from basalt and andesite. Within the parent-rock groupings the vanadium contents were generally highest at the clay stages and the element was considered to have concentrated to a small degree during soil weathering.

Strontium

From the ionic radii relationships of strontium and calcium, Goldschmidt (1954) considered that the early calcium minerals fractionating from magmas would be lower in strontium than the later sodium plagioclases and the earlier potassium feldspars. In the Skaergaard intrusion the strontium levels reached a maximum in the middle stages of fractionation (Wager and Mitchell, 1951).

In the weakly weathered topsoils the highest strontium contents were found in those derived from andesite. The leaching effects that accompanied weathering could, however, dominate the differences inherited from parent rock. The leaching ratios for strontium, obtained from the means of the weakly weathered and the strongly weathered soils, were 7 on ultrabasic, 46 on basalt, 31 on andesite, and 8 on rhyolite.

Barium

The ionic radius of barium is similar to that of potassium and allows substitutions to take place in potassium minerals. The barium contents of the weakly weathered topsoils were highest on rhyolite where the potassium levels were also at a maximum. Soil weathering was accompanied by losses of barium that amounted to leaching ratios of 9 on ultrabasic, 8 on basalt, 41 on andesite, and 23 on rhyolite.

Conclusions

Topsoils derived from basalts, andesites, and rhyolites, when only weakly weathered and low in organic matter, had total element contents that mostly followed the same distribution trends as magmatic fractionations.

Maximum Fe, Mg, Ca, Ti, Cr, Ni, Co, Mn in weakly weathered topsoils from basalt.
" Cu, V, Sr " " " andesite.
" Na, K, Zr, Ba " " " rhyolite.

When all stages of soil weathering were combined for establishing mean element contents of topsoils from the igneous rocks, ultrabasic, basalt, andesite, rhyolite, and granite, half the eighteen elements studied retained the same trends in distribution as in magmatic fractionations, although the actual levels had been modified by the soil-forming processes.

Maximum Fe, Mg, Cr, Ni, Co, Mn in topsoils from low silica igneous rocks.
" Na, K, Ba " " high " " "

By combining the element contents at all stages of soil weathering, the effects of leaching or concentration were superimposed on the levels

inherited from the rocks. Under the high rainfall conditions of the South-West Pacific region, soils at increasing degrees of weathering from their parent rocks showed a progressive loss of the bases Mg, Ca, Na, K, Sr, Ba. This resulted in a concentration, to a lesser degree, of the elements Fe, Ti, Mo, Ga, V, and slight, or irregular, changes in Al, Zr, Cr, Ni, Co, Mn, Cu. The leaching of elements has been expressed by the ratio of the mean element content of the weakly weathered topsoils to that of the strongly weathered topsoils, and the concentration ratio by mean content of the strongly weathered topsoils to that of the weakly weathered topsoils, within the parent-rock groupings.

Maximum leaching ratios were Sr 46, Ba 41, Ca 20, Na 20, Mg 15, K 8.
„ concentration „ „ Fe 3, Mo 3, Ga 3, Ti 2, V 2.

The levels of elements Al, Zr, Cr, Ni, Co, Mn, Cu showed no progressive change with increasing degree of soil weathering. Aluminium contents were high at the silt loam stage in all the parent-rock groupings, and in addition it concentrated at the clay stage on basalt. Zirconium concentrated on weathering up to the clay loam stage but, unlike titanium, concentration was not maintained at the clay stages. The elements Cr, Ni, Co were strongly fractionated during magmatic separation and the level of these elements in the topsoil can be used as an index of the soil's parent rock.

Podzolization by kauri litter of a soil from strongly weathered quartz-dacite rock resulted in a topsoil of high silica content and leached to a degree beyond that in the clay soils. Elements such as iron considered to concentrate by its resistance to being leached by predominantly climatic weathering processes had been removed from the topsoil by the vegetative leaching processes.

In the topsoils containing high amounts of organic matter, the organic had lower element contents (other than Mo, Sr), on an oven-dry weight basis, than the mineral-organic. Topsoils high in organic matter inherited, from its small mineral component, only the extremes of element distribution related to parent rock, Fe, K, Ti, Cr, Ni, Ba.

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REFERENCES

Birrell, K. S., and Wright, A. C. S. 1945. A serpentine soil in New Caledonia. N.Z. J. Sci. Tech. **27A**, 72–76.

Daly, R. A. 1933. Igneous Rocks and the Rocks of the Earth, pp. 9, 16, 17. McGraw-Hill, New York.

Fieldes, M. 1955. Clay mineralogy of New Zealand soils. Part 2. N.Z. J. Sci. Tech. **37B**, 336–50.

FIELDES, M., and SWINDALE, L. D. 1954. Chemical weathering of silicates in soil formation. N.Z. J. Sci. Tech. **36***B*, 140–54.

FUJIMOTO, G., and SHERMAN, D. G. 1950. Cobalt content of soils and plants of the Hawaiian Islands. J. Agron. **42,** 577–81.

GOLDSCHMIDT, V. M. 1954. Geochemistry. Ed. A. Muir. Clarendon Press, Oxford.

HOUGH, G. J., GILE, P. L., and FOSTER, Z. C. 1941. Rock weathering and soil profile development in the Hawaiian Islands. U.S.D.A. Tech. Bull. 752.

LOUNAMAA, J. 1956. Trace elements in plants growing wild on different rocks in Finland. Ann. Bot. Soc. Vanamo, **29,** No. 4.

MITCHELL, R. L. 1948. The spectrographic analyses of soils, plants and related minerals. Commonw. Bur. Soil Sci. Tech. Commun. 44.

ROBINSON, W. O., EDGINGTON, G., and BYERS, H. G. 1935. Chemical studies of infertile soils. U.S.D.A. Tech. Bull. 471.

SANDELL, E. B., and GOLDICH, S. S. 1943. The rarer metallic constituents of American igneous rocks. Part 2. J. Geol. **51,** 167–89.

TAYLOR, N. H. 1933. Soil processes in volcanic ash-beds. N.Z. J. Sci. Tech. **14,** 338–52.

—— 1948. Soil map of New Zealand. Soil Bur. Map S.B. 280.

—— CUNNINGHAM, I. J., and DAVIES, E. B. 1956. Soil type in relation to mineral deficiences. 7th Int. Grasslands Conf., New Zealand.

WAGER, L. R., and DEER, W. A. 1939. The petrology of the Skaergaard intrusion. Medd. om Grønland, **105,** 1–352.

—— and MITCHELL, R. L. 1951. The distribution of trace elements during strong fractionation of basic magma. Geochim. Cosmochim. Acta **1,** 129–208.

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FUJIMOTO, G., and SHERMAN, D. G. 1950. Cobalt content of soils and plants of the Hawaiian Islands. J. Agron. **42**, 577–81.
GOLDSCHMIDT, V. M. 1954. Geochemistry. Ed. A. Muir. Clarendon Press, Oxford.
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LOUNAMAA, J. 1956. Trace elements in plants growing wild on different rocks in Finland. Ann. Bot. Soc. Vanamo, **29**, No. 4.
MITCHELL, R. L. 1948. The spectrographic analyses of soils, plants and related minerals. Commonw. Bur. Soil Sci. Tech. Commun. 44.
ROBINSON, W. O., EDGINGTON, G., and BYERS, H. G. 1935. Chemical studies of infertile soils. U.S.D.A. Tech. Bull. 471.
SANDELL, E. B., and GOLDICH, S. S. 1943. The rarer metallic constituents of American igneous rocks. Part 2. J. Geol. **51**, 167–89.
TAYLOR, N. H. 1933. Soil processes in volcanic ash-beds. N.Z. J. Sci. Tech. **14**, 338–52.
—— 1948. Soil map of New Zealand. Soil Bur. Map S.B. 280.
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WAGER, L. R., and DEER, W. A. 1939. The petrology of the Skaergaard intrusion. Medd. om Grønland, **105**, 1–352.
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THE
JOURNAL OF SOIL SCIENCE

VOL. 11 SEPTEMBER 1960 NO. 2

CONTENTS

Dr. Robert Kenworthy Schofield 1901–1960 187

R. W. Jessup. The Stony Tableland Soils of the South-Eastern Portion of the Australian Arid Zone and their Evolutionary History . 188

R. W. Jessup. Identification and Significance of Buried Soils of Quaternary Age in the South-Eastern Portion of the Australian Arid Zone 197

M. J. Mulcahy. Laterites and Lateritic Soils in South-Western Australia 206

J. P. Andriesse. The Soils of Mazanderan in Northern Iran and their Suitability for Paddy-Rice Irrigation 226

J. A. R. Bates. Studies on a Nigerian Forest Soil. I. The Distribution of Organic Matter in the Profile and in Various Soil Fractions . 246

J. A. R. Bates *and* Mrs. T. C. N. Baker. Studies on a Nigerian Forest Soil. II. The Distribution of Phosphorus in the Profile and in Various Soil Fractions 257

S. A. Wilde *and* H. H. Krause. Soil-Forest Types of the Yukon and Tanana Valleys in Subarctic Alaska 266

R. Brewer. Cutans: their Definition, Recognition, and Interpretation 280

E. C. Childs. A Treatment of the Capillary Fringe in the Theory of Drainage. II. Modifications due to an Impermeable Sub-Stratum . 293

L. Leyton *and* J. S. P. Yadav. Effect of Drainage on Certain Physical Properties of a Heavy Clay Soil 305

E. L. Greacen. Water Content and Soil Strength 313

C. H. Williams, E. G. Williams, *and* N. M. Scott. Carbon, Nitrogen, Sulphur, and Phosphorus in Some Scottish Soils 334

D. J. Swaine *and* R. L. Mitchell. Trace-Element Distribution in Soil Profiles 347

A. E. Martin *and* R. Reeve. Chemical Studies of Podzolic Illuvial Horizons. IV. The Flocculation of Humus by Aluminium . . 369

A. E. Martin. Chemical Studies of Podzolic Illuvial Horizons. V. Flocculation of Humus by Ferric and Ferrous Iron and by Nickel 382

J. M. Bremner *and* D. S. Jenkinson. Determination of Organic Carbon in Soil. I. Oxidation by Dichromate of Organic Matter in Soil and Plant Materials 394

J. M. Bremner *and* D. S. Jenkinson. Determination of Organic Carbon in Soil. II. Effect of Carbonized Materials 403

N. Wells. Total Elements in Topsoils from Igneous Rocks: An Extension of Geochemistry 409

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